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The Mathematics of the Physical Properties of Crystals

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SECTION 1

INTRODUCTION

THE use of crystals as oscillating elements and as light valves in electric circuits has given the mathematics of crystalline media an engineering importance. Soon after the first simple quartz oscillators were made it was noticed that some ways of cutting the block from the natural crystal gave lower temperature coefficients of frequency than did other ways. This led to studies of the change of elastic modulii with direction and temperature and finally to the discovery that there are directions in quartz for which the shear modulus does not change with temperature.

Such computations are rather involved, and there is, in the English language, no general reference book on these new problems. The existing works were evidently not written with the idea in mind that anyone would ever actually do much numerical work with directional properties of crystals, since the methods used are not the best suited to this. The matrix algebra has the advantages of a symbolic algebra and is also, through the concept of matrix multiplication, a scheme for computing numerical results.

As the problem of temperature coefficients of frequency involves the temperature coefficient of expansion, the temperature coefficient of density and the temperature coefficient of elastic modulii, these problems must be put into the language of matrix algebra so that they will fit into the general structure being built for more difficult problems. For this reason, after an introduction to the idea of linear vector functions, through consideration of the relation between the electric field and the induction in a crystal, and a hasty sketch of symmetry types found in crystals, we proceed to the consideration of stress and strain and their relations to each other.

Following these, we take up piezo electricity and the converse piezo electric effects; these are important as they tell us the ways a crystal may be driven. We have not seen anywhere a general proof that the modulii of the converse effect are the same numbers as the modulii of the direct effect —to the first order of small quantities, though Lippman predicted the converse effect and demonstrated its magnitude to be about this; he ap-

parently didn't consider the general case of six simultaneous stress components, six strain components, three electric field components and three induction components. The fact that the mentioned relation is true only to the first order of small quantities seems to have escaped the attention of some experimenters who have sought to show non-linearity of the piezo-electric effect by demonstrating non-linearity in the converse effect.

As a basis for light valve problems, we handle the propagation of light through crystals, then the electro optic effect and the piezo optic effect.

SECTION 2

A Linear Vector Function

For almost every physical constant of an isotropic medium a crystalline medium has several constants. For instance, a piece of glass has a coefficient of thermal expansion but a crystal has many coefficients of thermal expansion, the coefficient depending on direction. It might be thought that there were no necessary relations between the coefficients in different directions but there are necessary relations.

As an example of the simplifying relations between the values of physical constants in different directions let us consider a crystal in an electric field. Measurements show that the dielectric constant varies with direction in a crystal. If the field is not in the direction of greatest dielectric constant, the displacement current might veer over a little, much as a nail tries to follow the grain of the wood. We shall assume that for any electric field vector E there corresponds an electric induction vector D which may not coincide with E. Also we assume that the magnitude of D is proportional to E, that is, if E results in D, then nE results in nD. Lastly, we assume that if E_1 results in D_1, E_2 in D_2 . . . and E_m results in D_m, then $E_1 + E_2 \ldots E_m$ results in $D_1 + D_2 + \ldots D_m$. If these assumptions hold, then as any arbitrary field E can be expressed as the vector sum of its three components E_1, E_2, E_3 along three arbitrary unit vectors i, j, k, the induction vector resulting from E can be computed from the induction vectors resulting from E_1, E_2, and E_3. For, let E_1 result in $D_{11}i + D_{21}j + D_{31}k$, E_2 result in $D_{12}i + D_{22}j + D_{32}k$ and E_3 result in $D_{13}i + D_{23}j + D_{33}k$, then $E_1 + E_2 + E_3 = E$ results in the induction vector:

$$\begin{aligned} D = \quad & (E_1D_{11} + E_2D_{12} + E_3D_{13})i \\ & + (E_1D_{21} + E_2D_{22} + E_3D_{23})j \\ & + (E_1D_{31} + E_2D_{32} + E_3D_{33})k \end{aligned} \quad \ldots\ldots\ldots\ldots (2.1)$$

It is seen then, that not more than 9 constants are needed to describe the dielectric properties of a crystal. The energy required to establish the

electric field is half the product of the component of the induction in the direction of the field and the electric field. This is, therefore:

$$2W = E_1^2 D_{11} + E_2^2 D_{22} + E_3^2 D_{33} + E_2 E_3 (D_{23} + D_{32}) + E_3 E_1 (D_{31} + D_{13}) + E_1 E_2 (D_{12} + D_{21})$$

Considering then a condenser made from a unit cube of crystal, the charge is D and the energy content is W. If there is no leakage loss, the charge that can be drawn from the condenser is $D = \frac{\partial W}{\partial E}$. Whence $D_1 = \frac{\partial W}{\partial E_1} = D_{11}E_1 + \frac{1}{2}(D_{12} + D_{21})\, E_2 + \frac{1}{2}\,(D_{13} + D_{31})\, E_3$. If, therefore, the induction is derivable from a potential, $D_{12} = \frac{1}{2}\,(D_{12} + D_{21})$ or $D_{12} = D_{21}$. Similarly $D_{13} = D_{31}$ and $D_{23} = D_{32}$. By a proper choice of axes the remaining six D's can be reduced to three. In the case of isotropic dielectrics $D_{11} = D_{22} = D_{33}$ and $4\pi D_{11}$ corresponds to k, the dielectric constant.

SECTION 3

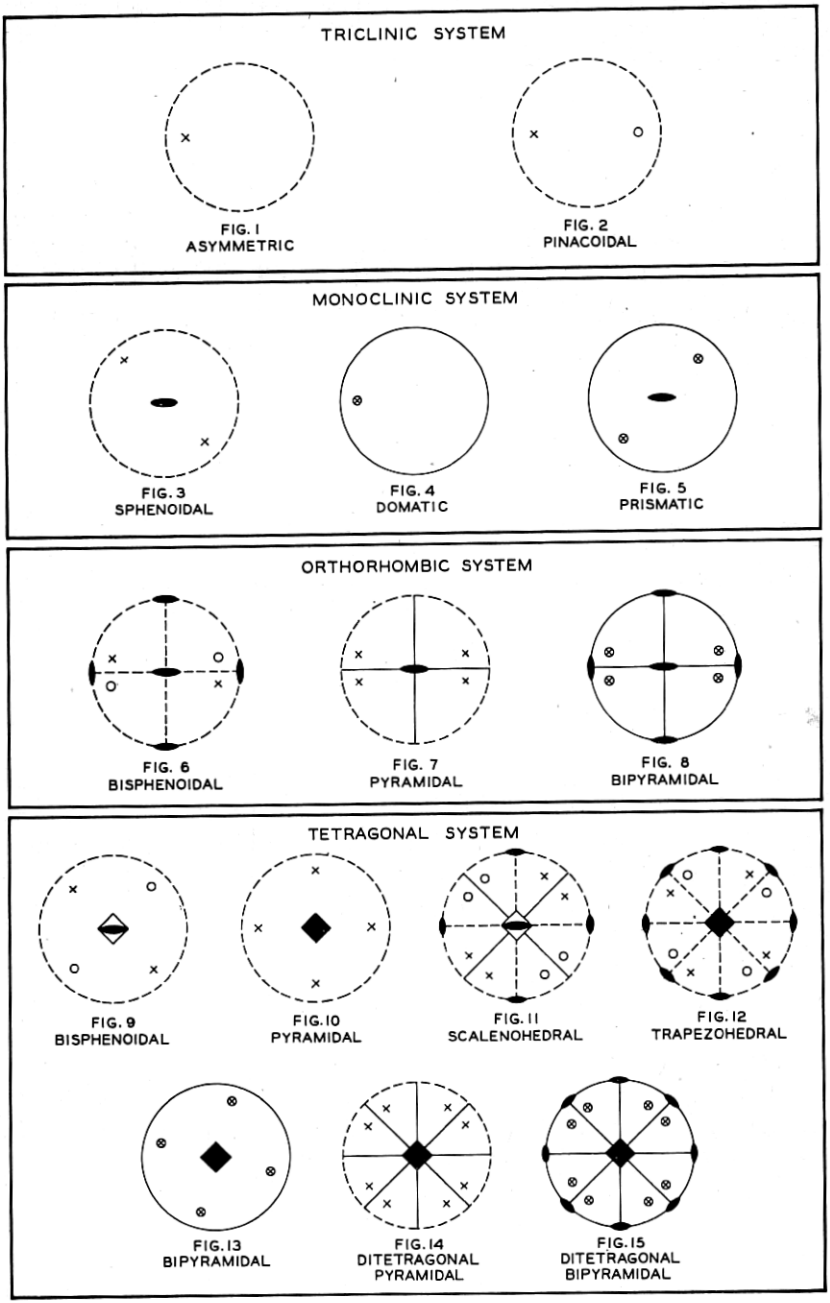
The Symmetry of Crystals

If a crystal has certain sorts of symmetry the number of constants required to describe each property is materially reduced. For this reason we now turn our attention to a study of symmetry.

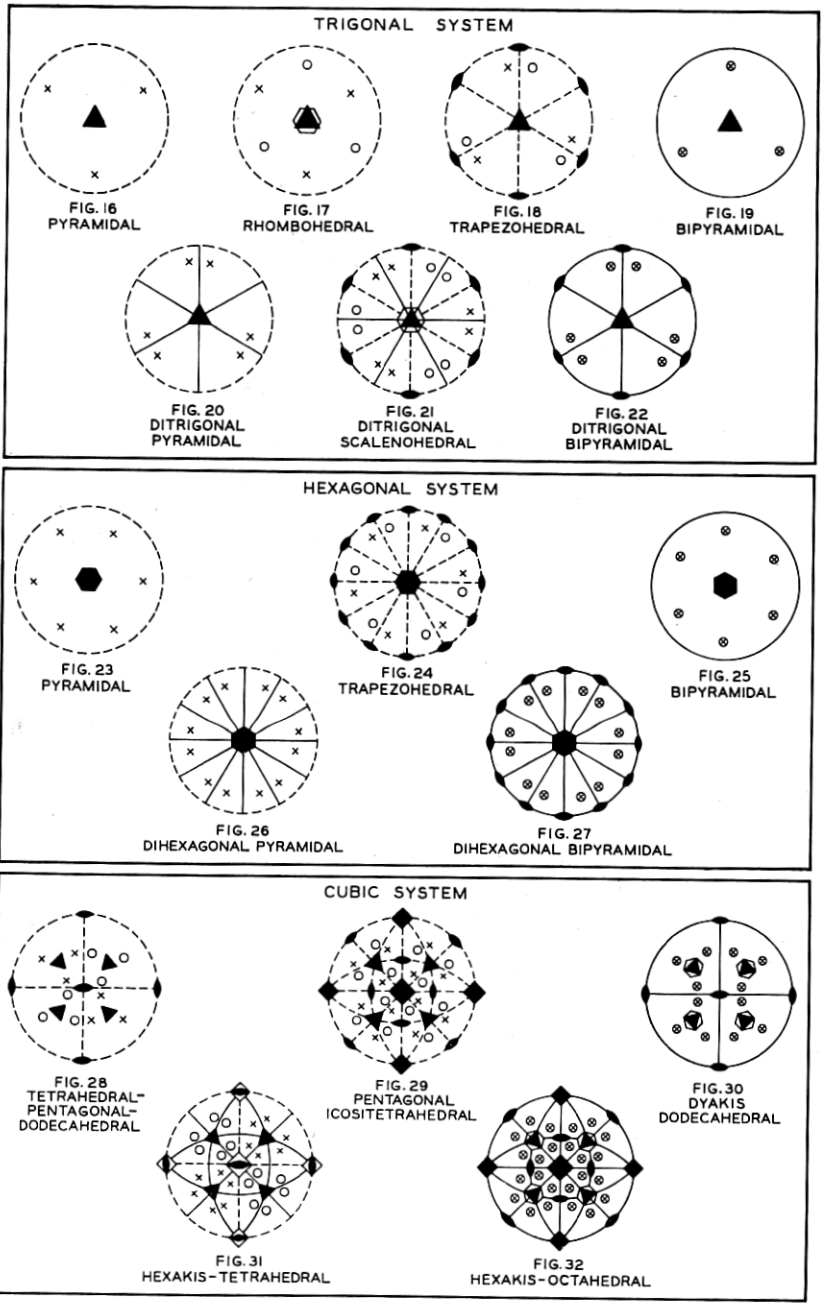
In general, plotting a vector property of the medium for a crystal gives a complicated surface which we shall call a property surface. Each property surface of a homogeneous isotropic medium is a sphere.

Because of the orderly arrangement of matter in a crystal, the property surfaces of crystalline media are commonly symmetrical. If a casting of a property surface were made it might fit into its mold in several positions. A property surface for quartz for example, if lifted from its mold and rotated through a third of a turn about the proper axis, would fit back into the mold. That is, quartz has a three fold axis. The natural requirement that molecules be laid down in a way economical of space limits the kinds of symmetry possible for crystals to axes of two fold (binary) symmetry, of three fold (trigonal), of four fold and of six fold symmetry, planes of reflection symmetry and combinations of axis-reflection symmetry, besides a simple symmetry through a center. From these elements it is possible to divide all possible property surfaces into 32 classes. No other classes built from these elements could be self-consistent.

A diagram study will prove this point. On a sphere let us mark axes of two fold symmetry by means of a solid boat shaped figure, three fold with a solid triangle, four fold with a square, six fold with a hexagon, planes of symmetry with a solid line (great circle) and combination axis reflection, by means of similar hollow figures. Finally, we shall project the sphere



Figs. 1–15—Crystal classes.



Figs. 16–32—Crystal classes.

and markings onto a plane through the center. Figures 1 to 32 is a set of such diagrams. Fig. 23 for instance shows a six fold axis. Fig. 1 represents a medium with no symmetry whatever. The cross represents a typical vector property, the vector piercing the sphere above the projection sheet. If the vector pierced below the sheet it would be marked with a circle. The dashed circle of Fig. 23 indicates the boundary of the sphere without implying it to be a plane of symmetry. The presence of six fold symmetry requires the typical vector to be shown in six places. If an axis of two fold symmetry is added at right angles to the six fold axis, it must appear six times and the typical vector must now appear twelve times, six times above and six times below the projection sheet. Continuing in this way we shall find the self-consistent classes of symmetry to be the 32 shown in the diagrams. Often the symmetry of a crystal class is expressed by means of a formula. A center of symmetry is symbolized by the letter C, a binary axis by A_2, a trigonal axis by A_3, a ternary axis by A_4, a six fold axis by A_6, a plane of reflection by P, and a combination rotation reflection by the combination symbols $\mathcal{A}_4$ or $\mathcal{A}_6$. In this way the symmetry formula of quartz for example, is $3A_2 \cdot A_3$.

SECTION 4

Matrix Algebra

In the solution of problems of crystal physics we are involved in the handling of many sets of linear simultaneous equations. As the matrix algebra lessens the work involved in handling sets of linear simultaneous equations we turn now to a study of matrix algebra.

Several independent variables $x_1, x_2 \ldots x_n$ are linearly related to several other independent variables $y_1, y_2 \ldots y_m$ as

$$\begin{aligned} y_1 &= a_{11}x_1 + a_{12}x_2 + \ldots a_{1n}x_n \\ y_2 &= a_{21}x_1 + \ldots \\ &\ldots\ldots\ldots\ldots\ldots\ldots \\ y_m &= a_{m1}x_1 + \ldots \quad a_{mn}x_n \end{aligned}$$

or briefly

$$y_l = \sum_{j=1}^{n} a_{lj}x_j \qquad l = 1, 2 \cdots m \ldots\ldots\ldots\ldots (4.1)$$

In most all such equations as (4.1) the variable to be summed over appears twice in the subscripts of one side. As a convention we agree to omit the summation sign and sum wherever subscripts are repeated.

Thus: $y_i = a_{ij}x_j$ is to be summed over j

again, if $x_j = b_{jk}z_k$ the z's being a third set of variables we have:

$$y_i = a_{ij}b_{jk}z_k \text{ to be summed over } j \text{ and } k.$$

We can think of this as a special multiplication of hyperquantities a, b and z. If we define

$$c_{ik} = a_{ij}b_{jk} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.2)$$

we may go from the y's to the z's directly thru $y_i = c_{ik}z_k$. We can now consider the "table"

$$\begin{pmatrix} a_{11}a_{12} \ldots a_n \\ a_{21} \ldots \\ a_{ml} \ldots a_{mn} \end{pmatrix}$$

as being the quantity a, and the table

$$\begin{pmatrix} b_{11}b_{12} \ldots\ldots b_m \\ \ldots\ldots\ldots \\ b_{pl} \quad \ldots\ldots b_{pm} \end{pmatrix}$$

as the quantity b.

These "tables" are called matrices.

Going to eq. (4.2) we see that the quantity c is to be a "table," the typical element c_{ij} of which is to be gotten by multiplying the ith row of a by the jth column of b, term by term thus:

$$c_{ij} = a_{i1}b_{ij} + a_{i2}b_{2j} + \ldots$$

After a little practice it becomes almost automatic to form the ijth term of the product of two matrices by letting the index finger of the left hand follow across the ith row of the left matrix while the right index finger follows down the jth column of the right matrix. The fingers step along in synchronism and at each pause the quantities under the two fingers are multiplied and the product added algebraically to the accumulated sum.

The algebra of these special multiplications is not commutable, i.e. $ab \neq ba$.

Eq. (4.1) can be considered as a special case of eq. (4.2), in which the matrices x and y have one column only. In this manner a vector with components x_1 x_2 x_3 can be considered as the matrix $\begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix}$.

If eq. (4.1) has the same number of x's as y's we may solve (by means of determinants) for the x's in terms of the y's. We would then get a new set of equations

$$x_i = a_{ij}^{-1}\, y_j.$$

The significance of the a^{-1} is that the matrix product of a and a^{-1} is a matrix with ones on the major diagonal and all other terms zero. Whenever the product of two square matrices gives such a matrix (known as the idemfactor, I) they are said to be reciprocal. Only square matrices have reciprocals. Multiplying any matrix by the idemfactor leaves the matrix unchanged. We might consider, as part of our mathematical short hand, that eq. (4.1) was solved for x by multiplying through by a^{-1}, as

$$a^{-1}y = a^{-1}ax = Ix = x.$$

We must remember that the order must not be disturbed as the quantities are not commutable, and that only square matrices have reciprocals.

The major diagonal of a square matrix is the set of terms running diagonally from the upper left to the lower right.

A symmetrical matrix has any term $M_{ij} = M_{ji}$

An anti-symmetric or skew symmetric matrix has any term $M_{ij} = -M_{ji}$ for $i \neq j$.

Rotation Theory

The matrix algebra can be used to express a vector as a function of another vector, that is to handle such relations as exist between E and P of section 2.

There is another important aspect of matrix multiplication, that of transforming a function from one set of axes to another. Let us assume that the new set of unit axes, x_1' x_2' and x_3' are merely the old ones rotated through angle ϕ about some axis A which is a unit vector passing through the origin. From Fig. 33 we see that in the expression:

$$x_1 = a_{11}x_1' + a_{21}x_2' + a_{31}x_3'$$

the a_{ij}'s are the cosines of the angles between x_1 and the three quantities x_j'. Conversely they are the cosines of the angles between the x_j''s and x_1. Consequently, if the primed unit vectors are given in terms of the unprimed ones by the three equations

$$x_i' = a_{ij}x_j$$

then the unprimed x's are given in terms of the primed ones by the expression:

$$x_j = a_{ji}x_i'$$

This reversible relationship is well depicted by the table:

	x_1	x_2	x_3
x_1'	a_{11}	a_{12}	a_{13}
x_2'	a_{21}	a_{22}	a_{23}
x_3'	a_{31}	a_{32}	a_{33}

In this direction cosine table we can "look up" the components of any unit vector in terms of the other system.

The matrix a_{ji} is merely the matrix a_{ij} with rows and columns interchanged. a_{ji} is called the conjugate of a_{ij}. We shall denote the conjugate of any matrix M by M_c.

Obviously V' is the vector sum of the 3 components (on the new system) of each of its 3 components on the old system.

$$(V)_{\text{new}} = \begin{pmatrix} a_{11}^{-1}V_1 + a_{12}^{-1}V_2 + a_{13}^{-1}V_3 \\ a^{-1}\,V + \cdots\cdots\cdots\cdots, \\ \cdots \qquad \cdots \qquad \cdots \end{pmatrix}$$

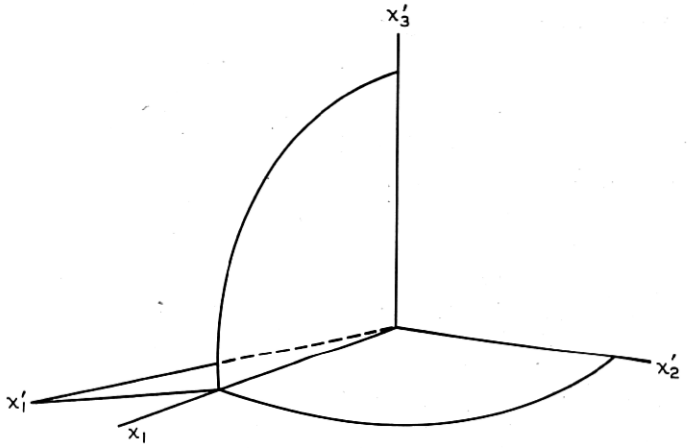


Fig. 33—The direction cosines of X_1 on $X'_1\ X'_2\ X'_3$.

If the expression giving the components of V on the new system is denoted by V' we may write

$$V' = a\,V$$

conversely

$$V = a^{-1}\,V'$$

Since x_1 is of unit length, the sum of the squares of its three components (on the primed system) is unity.

That is

$$a_{11}^2 + a_{12}^2 + a_{13}^2 = 1$$

similarly

$$a_{21}^2 + a_{22}^2 + a_{23}^2 = 1 \qquad (4.3)$$

and

$$a_{31}^2 + a_{32}^2 + a_{33}^2 = 1$$

Now a_c can be considered as a rotation similar to the rotation a. Consequently their product aa_c is a similar rotation. Let us consider this product.

The squares of its terms must sum to zero, row by row as in (4.3)

$$\begin{pmatrix} a_{11}a_{12}a_{13} \\ a_{21}a_{22}a_{23} \\ a_{31}a_{32}a_{33} \end{pmatrix} \begin{pmatrix} a_{11}a_{21}a_{31} \\ a_{12}a_{22}a_{32} \\ a_{13}a_{23}a_{33} \end{pmatrix} = \begin{pmatrix} 1 & . & . \\ . & 1 & . \\ . & . & 1 \end{pmatrix}$$

Because of the relations $a_{11}^2 + a_{12}^2 + a_{13}^2 = 1$, etc., we see that the terms of the third matrix are zero for all terms not on the major diagonal. Therefore, aa_c is an idemfactor and the reciprocal matrix of a is the same as its conjugate matrix.

$$a_c = a^{-1} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.4)$$

Also x_1' is of unit length, and the sum of the squares of its components on the unprimed system is unity. Thus we find:

$$\begin{aligned} a_{11}^2 + a_{21}^2 + a_{31}^2 &= 1 \\ a_{12}^2 + a_{22}^2 + a_{32}^2 &= 1 \\ a_{13}^2 + a_{23}^2 + a_{33}^2 &= 1 \end{aligned} \quad \ldots\ldots\ldots\ldots\ldots\ldots (4.5)$$

We now introduce from vector analysis the concept of the scalar product. The scalar product of two vectors u and v is $u_c v$. It is the product of the lengths of the two vectors and the cosine of the angle between them.

If we take the scalar product of x_1 and x_2 as expressed in the primed system we have, since they are mutually perpendicular:

$$(a_{11}, a_{12}, a_{13}) \begin{pmatrix} a_{21} \\ a_{22} \\ a_{23} \end{pmatrix} = a_{11}a_{21} + a_{12}a_{22} + a_{13}a_{23} = 0$$

Similarly multiplying x_2 and x_3 scalarly, and x_3 and x_1 we find:

$$\begin{aligned} a_{11}a_{21} + a_{12}a_{22} + a_{13}a_{23} &= 0 \\ a_{21}a_{31} + a_{22}a_{32} + a_{23}a_{33} &= 0 \\ a_{31}a_{11} + a_{32}a_{12} + a_{33}a_{13} &= 0 \end{aligned} \quad \ldots\ldots\ldots\ldots\ldots\ldots (4.5)$$

If we multiply x_1' and x_2' etc. as expressed on the unprimed system we get the relations:

$$\begin{aligned} a_{11}a_{12} + a_{21}a_{22} + a_{31}a_{32} &= 0 \\ a_{12}a_{13} + a_{22}a_{23} + a_{32}a_{33} &= 0 \\ a_{13}a_{11} + a_{23}a_{21} + a_{33}a_{31} &= 0 \end{aligned} \quad \ldots\ldots\ldots\ldots\ldots\ldots (4.7)$$

The vector product of two vectors u and v requires the defining of a special matrix, the cross matrix.

$$u \times = \begin{pmatrix} 0 & -u_3 & u_2 \\ u_3 & 0 & -u_1 \\ -u_2 & u_1 & 0 \end{pmatrix} \quad \ldots\ldots\ldots\ldots\ldots\ldots (4.8)$$

We note that this is formed by writing zeros on the major diagonal, then going back from the lower right corner writing u_1, u_2 and u_3 around the edges. We then make the lower left term negative, then operate on the opposite side of the major diagonal so as to make the matrix skew symmetric.

The reciprocal of any matrix m is

$$m_{ij}^{-1} = \frac{M_{ji}(-1)^{i+j}}{|m|} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.9)$$

where M_{ji} is the ji minor of $|m|$.

The cross matrix has no reciprocal as for it (4.9) becomes indeterminate.

Since the vector product of two vectors u and v is another vector perpendicular to both u and v and of a length uv sin (uv) we may write, on the primed system

$x_1 \times x_2 = x_3$ in the form

$$\begin{pmatrix} 0 & -a_{13} & a_{12} \\ a_{13} & 0 & -a_{11} \\ -a_{12} & a_{11} & 0 \end{pmatrix} \begin{pmatrix} a_{21} \\ a_{22} \\ a_{23} \end{pmatrix} = \begin{pmatrix} -a_{13}a_{22} + a_{12}a_{23} \\ a_{13}a_{21} - a_{11}a_{23} \\ -a_{12}a_{21} + a_{11}a_{22} \end{pmatrix} = \begin{pmatrix} a_{31} \\ a_{32} \\ a_{33} \end{pmatrix}$$

Matrices including vectors are equal only when their corresponding terms are equal. Hence, we get the relations

$$\begin{aligned} a_{31} &= a_{12}a_{23} - a_{13}a_{22} \\ a_{32} &= a_{13}a_{21} - a_{11}a_{23} \\ a_{33} &= a_{11}a_{22} - a_{12}a_{21} \end{aligned} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.10)$$

Similarly we get the relations:

$$\begin{aligned} a_{11} &= a_{22}a_{33} - a_{23}a_{32} \\ a_{12} &= a_{23}a_{31} - a_{21}a_{33} \\ a_{13} &= a_{21}a_{32} - a_{22}a_{31} \\ a_{21} &= a_{32}a_{13} - a_{12}a_{33} \\ a_{22} &= a_{33}a_{11} - a_{31}a_{13} \\ a_{23} &= a_{31}a_{12} - a_{32}a_{11} \end{aligned} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.11)$$

The 21 relations between the a_{ij}'s allow us to complete the matrix given four terms.

Several Useful Matrix Relations

The del operator is the pseudo vector $\nabla = \begin{pmatrix} \partial/\partial\, x_1 \\ \partial/\partial\, x_2 \\ \partial/\partial\, x_3 \end{pmatrix} \ldots\ldots\ldots\ldots (4.12)$

It transforms upon a rotation of axes as does an ordinary vector:

$$\nabla' = a\nabla \quad (4.13)$$

$$\text{grad } u = \nabla u_c, \text{ a matrix} \quad (4.14)$$

$$\text{div } u = \nabla_c u, \text{ a scalar} \quad (4.15)$$

$$\text{curl } u = \nabla \times u, \text{ a matrix} \quad (4.16)$$

$$\text{grad radius vector} = \nabla\rho = I, \text{ the idemfactor} \quad (4.17)$$

$$(abc\ldots)^{-1} = \ldots c^{-1}b^{-1}a^{-1} \quad (4.18)$$

$$(abc\ldots)_c c = \ldots c_c b_c a_c \quad (4.19)$$

$$\begin{pmatrix} a_{11} & 0 & 0 & 0\ldots \\ 0 & a_{22} & 0 & 0\ldots \\ 0 & 0 & a_{33} & \ldots\ldots \\ \ldots\ldots\ldots & & & \end{pmatrix}^{-1} = \begin{pmatrix} 1/a_{11} & 0 & 0 & \ldots \\ 0 & 1/a_{22} & 0 & \ldots \\ 0 & 0 & 1/a_{33} & \ldots \\ \ldots & \ldots & \ldots & \ldots \end{pmatrix} \quad (4.20)$$

$$(\text{Scalar times matrix})^{-1} = \frac{(\text{matrix})^{-1}}{\text{scalar}} \quad (4.21)$$

SECTION 5

The Geometry of Rotations

As a first application of the matrix algebra let us compute the a matrix for a few general rotations. Although we can consider a general rotation as one of angle ϕ about the unit vector* A, it is easier to consider a general rotation as three successive rotations about coordinate axes.

A study of Fig. 34 shows that for a counterclockwise rotation ϕ about x_1, the new components of a vector V are:

$$\begin{aligned} V_1' &= V_1 \\ V_2' &= V_2 \cos\phi + V_3 \sin\phi \\ V_3' &= -V_2 \sin\ \phi + V_3 \cos\phi \end{aligned}$$

whence $V' = aV$ where

$$a = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\phi & \sin\phi \\ 0 & -\sin\phi & \cos\phi \end{pmatrix} \quad (5.1)$$

* A general rotation of amount ϕ about the unit axis A is given by

$$a = AA_c + (I - AA_c)\,\text{Cos}\,\phi + \text{Sin}\,\phi\, A$$

See Vector Analysis (Gibbs Wilson, Yale Press) pp. 338.

Similarly, for a counterclockwise rotation ϕ about x_2 we have

$$a = \begin{pmatrix} \cos\phi & 0 & -\sin\phi \\ 0 & 1 & 0 \\ \sin\phi & 0 & \cos\phi \end{pmatrix} \quad \ldots\ldots\ldots\ldots\ldots\ldots (5.2)$$

and for a counterclockwise rotation ϕ about x_3:

$$a = \begin{pmatrix} \cos\phi & \sin\phi & 0 \\ -\sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \ldots\ldots\ldots\ldots\ldots\ldots (5.3)$$

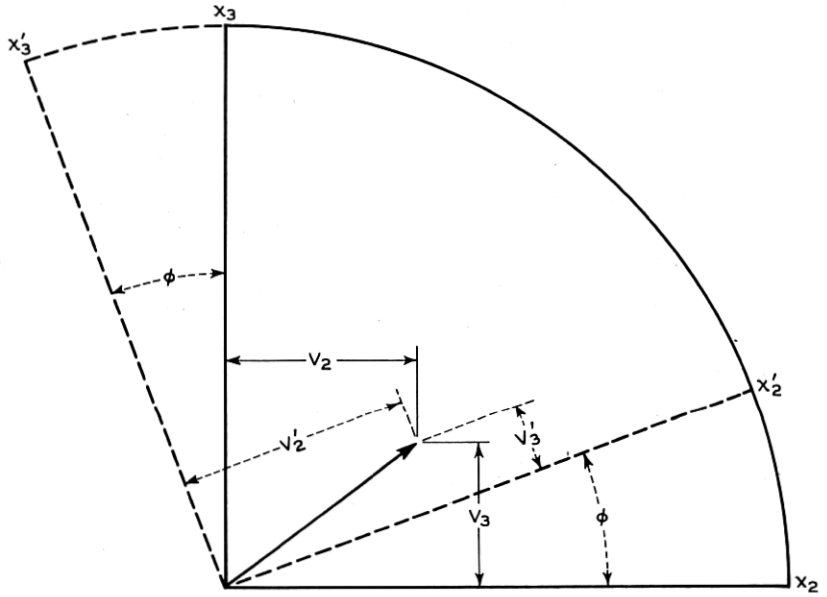


Fig. 34—The relationship between the components of a vector on one coordinate system and on another.

In the appendix we give the special transformations corresponding to the symmetry operations of the 32 crystal classes. If we have three successive rotations:

$$x' = ax$$
$$x'' = a'x'$$
$$x''' = a''x''$$

the resultant rotation is

$$x''' = a''a'ax$$

or

$$x''' = Rx \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5.4)$$

where

$$R = a''a'a \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5.5)$$

The I.R.E. Orientation Angles and the I.R.E. Matrix

The Institute of Radio Engineers has proposed that, for quartz crystals, all orientations be given in terms of three rotations ϕ, θ, ψ about x_3, x_2' and x_3'' respectively, starting with the plate length along x_1 width along x_2 and thickness along x_3. (Here x_3 is the z or optic axis, x_1 is the electric axis.)

Whence, here:

$$R = \begin{pmatrix} \cos\psi & \sin\psi & 0 \\ -\sin\psi & \cos\psi & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \cos\theta & 0 & -\sin\theta \\ 0 & 1 & 0 \\ \sin\theta & 0 & \cos\theta \end{pmatrix} \begin{pmatrix} \cos\phi & \sin\phi & 0 \\ -\sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

and carrying out the two matrix multiplications:

$$\begin{array}{c} \begin{array}{ccc} x_1 & x_2 & x_3 \end{array} \\ \left(\begin{array}{lll} \cos\phi\cos\theta\cos\psi & \sin\phi\cos\theta\cos\psi & -\sin\theta\cos\psi \\ \quad -\sin\phi\sin\psi & \quad +\cos\phi\sin\psi & \end{array} \right. \\ \left. \begin{array}{lll} -\cos\phi\cos\theta\sin\psi & -\sin\phi\cos\theta\sin\psi & \\ \quad -\sin\phi\cos\psi & \quad +\cos\phi\cos\psi & \sin\theta\sin\psi \\ \cos\phi\sin\theta & \sin\phi\sin\theta & \cos\theta \end{array} \right) \end{array} \begin{array}{l} x_1''' \\ \\ \\ x_2''' \\ \\ x_3''' \end{array} \quad \ldots(5.6)$$

If we denote the unit vectors along the length, width and thickness as P_1P_2 and P_3 respectively we have as a matrix defining the plate:

$$P = Rx \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5.7)$$

The I.R.E. orientation system is useful to the designer of crystal plates because his problem is to choose such values of ϕ, θ, ψ as to give the plate certain physical properties along its length, width and thickness. The man who cuts the plate has a different problem, that of moving the crystal (and hence the x_1 x_2 x_3 axes) about a fixed saw so that the plate cut parallel to the saw blade is what the designer ordered.

Let us consider such a system as shown in Figs. 37, 38 and 39. In Fig. 38 the crystal stands with its optic axis along P_3, its + electric axis (for right hand quartz) along P. Since the shop man considers clockwise rotation as positive we now rotate the crystal through angle U_3 about P_3 clockwise, we then turn the crystal through angle U_2 clockwise about P_1, and finally, after cutting out a slab of required thickness, we turn it clockwise through angle U_1 about P_3 to cut its length and width.

On the plate axes P_1 the crystallographic axes x_1 x_2 x_3 are now given by

$$x = rP \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5.8)$$

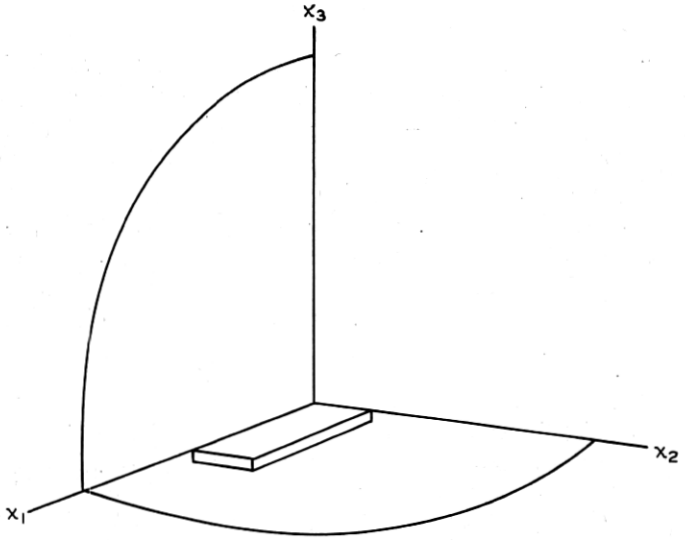


Fig. 35—The initial position (0, 0, 0) for the I.R.E. direction angles.

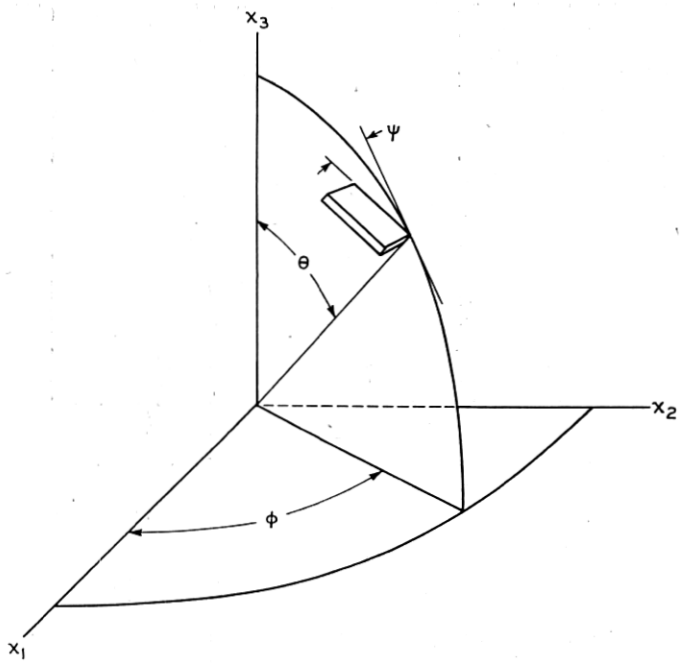


Fig. 36—The final position (Φ, Θ, Ψ) for the I.R.E. direction angles.

where

$$r = \begin{pmatrix} \cos U_1 & \sin U_1 & 0 \\ -\sin U_1 & \cos U_1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & \theta & \theta \\ 0 & \cos U_2 & \sin U_2 \\ 0 & -\sin U_2 & \cos U_2 \end{pmatrix} \begin{pmatrix} \cos U_3 & \sin U_3 & 0 \\ -\sin U_3 & \cos U_3 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

or

$$r = \begin{pmatrix} \cos U_1 \cos U_3 & \cos U_1 \sin U_3 & \sin U_1 \sin U_2 \\ -\sin U_1 \cos U_2 \sin U_3 & +\sin U_1 \cos U_2 \cos U_3 & \\ -\sin U_1 \cos U_3 & -\sin U_1 \sin U_3 & \cos U_1 \sin U_2 \\ -\cos U_1 \cos U_2 \sin U_3 & +\cos U_1 \cos U_2 \cos U_3 & \\ \sin U_2 \sin U_3 & -\sin U_2 \cos U_3 & \cos U_2 \end{pmatrix} \quad (5.9)$$

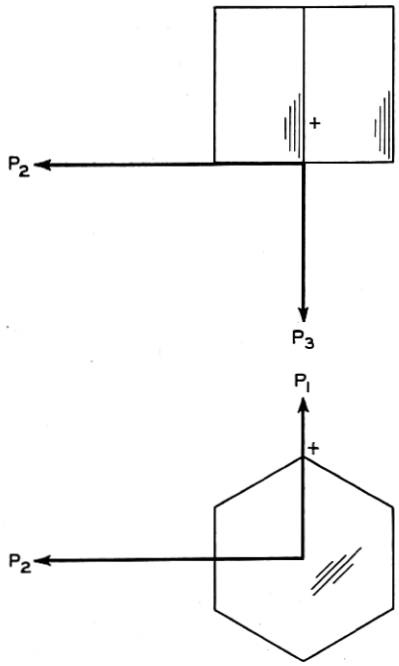


Fig. 37

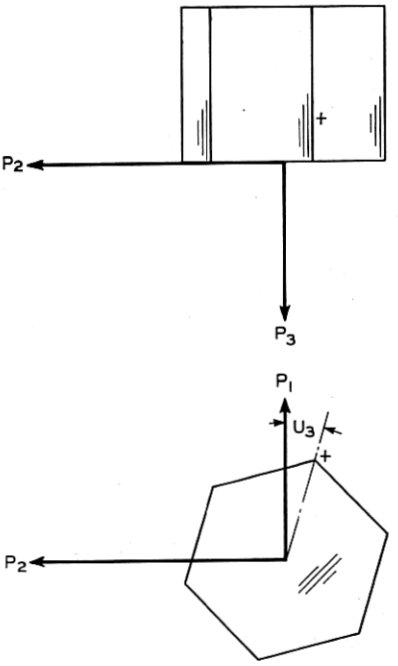


Fig. 38

Fig. 37—The (0, 0, 0) position of a shop system of direction angles.
Fig. 38—The second position of a shop system.

From (5.8) we see that $P = rx$ and hence, if this is to be the same plate the designer specified by $P = Rx$ we must have $R = r$ whence we may equate the terms of (5.6) and (5.9) to get the relations

$$\begin{aligned} \cos U_2 &= \cos\theta \text{ or } U_2 = \pm\theta \\ \tan U_1 &= \cot\psi \\ \tan U_3 &= \cot\phi \end{aligned} \qquad (5.10)$$

or

$$\begin{aligned} U_1 &= \psi - 90 + n\pi \\ U_2 &= \theta \\ U_3 &= \phi - 90 + n\pi \end{aligned}$$

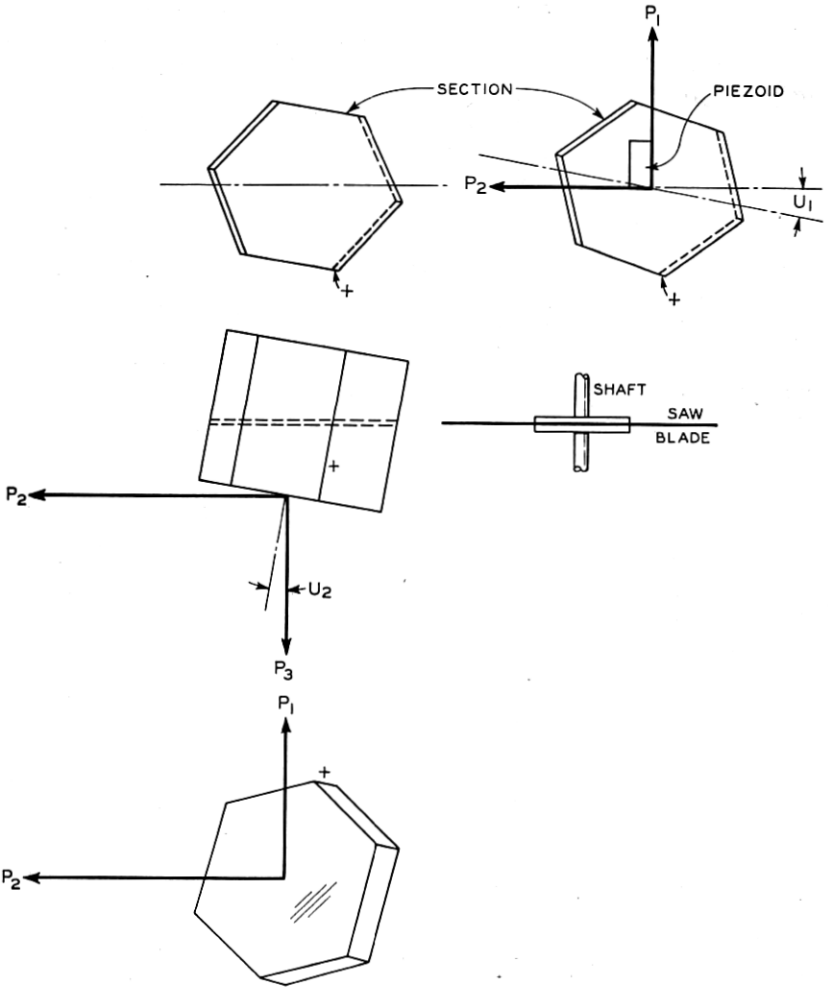


Fig. 39—Cutting the slab and trimming it to the piezoid boundaries.

Where n is any integer positive or negative, including zero. If we take

$$\begin{aligned} U_1 &= \psi - 90 \\ U_2 &= \theta \\ U_3 &= \phi + 90 \end{aligned} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (5.11)$$

The matrices are consistent term by term.

SECTION 6

Crystalline Dielectrics

As a first application of the matrix algebra considered as a linear vector function let us reconsider the problem of the crystal in an electric field.

The relations of chapter II, equation (1) can be written in the abbreviated form:

$$D = D_{ij}E \qquad \text{where} \qquad D_{rs} = D_{sr}$$

in accordance with the system of abbreviations adopted in the appendix.

If we put

$$4\pi D_{rs} = k_{rs}$$

equation (1) can be written

$$D = \frac{1}{4\pi} k_{rs} E \ldots\ldots\ldots\ldots\ldots\ldots (6.1)$$

In order to investigate the effects of crystal symmetry in determining the least number of dielectric constants that are required for a given class of symmetry it is desirable to find the electric induction D for any system of axes. Suppose that we choose a system for axes x_1', x_2', x_3' related to x_1, x_2, x_3 through the relations:

$$\begin{aligned} x_1 &= a_{11}x_1' + a_{12}x_2' + a_{13}x_3' \\ x_2 &= a_{21}x_1' + a_{22}x_2' + a_{23}x_3' \\ x_3 &= a_{31}x_1' + a_{32}x_2' + a_{33}x_3' \end{aligned} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (6.2)$$

where a_{11} is the cosine of the angle between x_1 and x_1', a_{12} is the cosine of the angle between x_1' and x_2 etc.

Equation (6.2) can be abbreviated to

$$x' = ax$$

where a is the matrix

$$a = \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix}$$

It is shown in the sec. 4 that any vector $V = \begin{pmatrix} V_1 \\ V_2 \\ V_3 \end{pmatrix}$ can be written on the new system of axes as V' where $V' = aV$, conversely $V = a^{-1}V'$; a^{-1} is the matrix reciprocal to a. Since the induction D and the electric field E are simple vector functions they transform as the vector V, that is:

$$D' = aD \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6.3)$$

$$E' = aE \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6.4)$$

But by (6.1)

$$D = \frac{1}{4\pi} kE$$

whence:

$$aD = \frac{1}{4\pi} aka_c aE$$

or

$$D' = \frac{1}{4\pi} k'E' \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6.5)$$

if

$$k' = aka_c \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6.6)$$

We see that the form of (6.5) is the same as that of (6.1) for any set of axes if (6.6) is used to define the new dielectric matrix k.

To apply this relation (6.6) to a particular crystal let us consider a tetragonal crystal (which has its properties unchanged by a rotation of 90° about a four fold axis). Let us choose the four fold axis as x_3 and then rotate the axis 90° about x_3. In this case

$$a = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \text{ and the reciprocal matrix } a^{-1} = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

whence equation (6.6) becomes:

$$k' = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} k_{11} & k_{12} & k_{31} \\ k_{12} & k_{22} & k_{23} \\ k_{31} & k_{23} & k_{33} \end{pmatrix} \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} k_{22} & -k_{12} & k_{23} \\ -k_{12} & k_{11} & -k_{31} \\ k_{23} & -k_{31} & k_{33} \end{pmatrix}$$

But because of the symmetry k is unchanged by this transformation, hence

$$k = k'$$

Two matrices can be equal only if corresponding terms are equal, hence

$$k_{11} = k_{22}\,,\ k_{12} = -k_{12} = 0,\ k_{23} = -k_{31} \text{ and } k_{31} = k_{23}$$

whence

$$k_{23} = k_{31} = 0.$$

We are left then, with the dielectric constant matrix for the tetragonal bisphenoidal class:

$$k = \begin{pmatrix} k_{11} & 0 & 0 \\ 0 & k_{11} & 0 \\ 0 & 0 & k_{33} \end{pmatrix}$$

Applying other transformations possible for tetragonal crystals gives no further simplification.

If we go through all the symmetry transformations possible for the 32 classes we find that cubic crystals require but one dielectric constant, hexagonal, trigonal and tetragonal crystals require two constants, orthorhombic monoclinic and triclinic crystals require 3.

As the triclinic class has no fixed axes or planes of symmetry the reduction of its 6 constants to 3 is not so obvious. It may be seen by expanding into ordinary xyz coordinates, that $\rho_c k \rho = 1$ is the equation of an ellipsoid, (ρ is the radius vector) where the six k's are the coefficients of x^2, y^2, z^2, yz, zx and xy respectively. If we choose the coordinate axes along the axes of the ellipsoid the yz, zx and xy terms drop out and only three k's are needed. With triclinic crystals then, if we determine the axes of the ellipsoid, then choose the coordinate axes along them, only three dielectric constants are needed to completely specify the polarization in terms of the electric field. The determination of the ellipsoid axes must be made experimentally as there are no symmetry elements to guide us. It is possible to compute the positions of the axes from the 6 k's by solving a cubic equation.

The values of the k's depend on the frequency of the applied field. In crystals of low symmetry the ellipsoid axes for different frequencies do not necessarily coincide.

Another vector quantity of interest is the polarization, $P = D - \frac{1}{4\pi} E$.

Using (1) this becomes

$$P = \frac{1}{4\pi}(k - I)E \quad \ldots\ldots\ldots\ldots\ldots\ldots (6.7)$$

SECTION 7

Quadratic Forms

Often the elements of a matrix are themselves functions of other quantities. In order to relate the elements of one matrix with those of another by means of a matrix multiplication, we may make a single column matrix of each of them. We then wish to know how a transformation of axes changes the elements of this single column matrix. Consider a symmetrical matrix b that relates two vectors u and v:

$$u = bv.$$

A transformation of axes, a, changes u and v to u' and v'. Multiplying $u = bv$ through by the prefactor a we have

$$au = abv.$$

We now replace au by its equivalent $a^{-1}v'$ whence:

$$u' = aba^{-1}v'$$

so that

$$u' = b'v'$$

if we define b' as

$$b' = aba^{-1} \quad \ldots\ldots\ldots\ldots\ldots\ldots (7.1)$$

To be in accord with common usage we now rearrange b according to the arbitrary scheme:

$$\begin{pmatrix} b_{11} \\ b_{22} \\ b_{33} \\ b_{23} \\ b_{31} \\ b_{12} \end{pmatrix} = \begin{pmatrix} B_1 \\ B_2 \\ B_3 \\ . \\ . \\ B_6 \end{pmatrix}$$

We wish to know what operation to perform on B to get B' corresponding to b'. If we expand $b' = aba^{-1}$ it is easily seen that $b' = \alpha B$ where

$$\alpha = \begin{pmatrix} a_{11}^2 & a_{12}^2 & a_{13}^2 & 2a_{12}a_{13} & 2a_{13}a_{11} & 2a_{11}a_{12} \\ a_{21}^2 & a_{22}^2 & a_{23}^2 & 2a_{22}a_{23} & 2a_{23}a_{21} & 2a_{21}a_{22} \\ a_{31}^2 & a_{32}^2 & a_{33}^2 & 2a_{32}a_{33} & 2a_{33}a_{31} & 2a_{31}a_{32} \\ a_{21}a_{31} & a_{22}a_{32} & a_{23}a_{33} & a_{22}a_{33} + a_{23}a_{32} & a_{21}a_{33} + a_{23}a_{31} & a_{22}a_{31} + a_{21}a_{32} \\ a_{31}a_{11} & a_{32}a_{12} & a_{33}a_{13} & a_{12}a_{33} + a_{13}a_{32} & a_{13}a_{31} + a_{11}a_{33} & a_{11}a_{32} + a_{12}a_{31} \\ a_{11}a_{21} & a_{12}a_{22} & a_{13}a_{23} & a_{12}a_{23} + a_{13}a_{22} & a_{13}a_{21} + a_{11}a_{23} & a_{11}a_{22} + a_{12}a_{21} \end{pmatrix} \quad \ldots(7.2)$$

Because we shall often need to form the α matrix from the a matrix we need an easily remembered mechanism for doing so. We notice that those are four kinds of terms in the α matrix and that the four kinds can be separated from each other by two center lines, one horizontal, one vertical. This gives us four squares of nine terms each and we can correlate each term of any square to a term of the a matrix by means of its position in the square. The terms of the upper left square are the squares of the corresponding terms of the a matrix. To form any term of the lower left square we cover the corresponding term of the a matrix with our finger and multiply the visible terms of that column. To form any term of the upper right square we cover the corresponding a term and write down *double* the product of the visible terms of that row. To form any term of the lower right square we find the corresponding a term, strike out that row and column and write down the *sum* of the remaining cross products. A study of the following diagram will help to remember these rules.

Terms are squares of corresponding a terms	Omission products doubled
Omission products	Sum of omission cross products

Fig. 40

SECTION 8

Crystal Elasticity

Stress

Consider a point P in a medium acted on by forces. If a small area is chosen about P the medium on one side of the area exerts a force on the medium on the other side. The force will depend on the size of the area and

on the direction of its normal n. We shall choose a triangular area ds such that an arbitrarily chosen set of mutually perpendicular unit axes x_1, x_2, x_3 pass through the vertices of the triangle. Let us consider the conditions of equilibrium of the tetrahedral element of volume so formed. The areas normal to x_1, x_2, x_3 are ds_1, ds_2, ds_3, respectively, and the forces per unit area acting through these faces are:

$$F_1 = \begin{pmatrix} f_{11} \\ f_{12} \\ f_{13} \end{pmatrix}, \qquad F_2 = \begin{pmatrix} f_{21} \\ f_{22} \\ f_{23} \end{pmatrix}, \qquad F_3 = \begin{pmatrix} f_{31} \\ f_{32} \\ f_{33} \end{pmatrix}$$

Any body forces (such as gravity) depend on a higher order of smallness (that is on the volume rather than on the area) and hence are negligible. Whence for equilibrium:

$$Fds = F_1 ds_1 + F_2 ds_2 + F_3 ds_3$$

But

$$ds_1 = n_1 ds, \qquad ds_2 = n_2 ds \qquad \text{and} \qquad ds_3 = n_3 ds$$

where $\begin{pmatrix} n_1 \\ n_2 \\ n_3 \end{pmatrix}$ is the normal to the area ds. Whence we may write: $F = fn$ where f is the matrix

$$\begin{pmatrix} f_{11} f_{12} f_{13} \\ f_{21} f_{22} f_{23} \\ f_{31} f_{32} f_{33} \end{pmatrix}$$

For the body to be in rotational equilibrium the tangential forces must balance, hence $f_{12} = f_{21}$, $f_{13} = f_{31}$ and $f_{23} = f_{32}$.

Transformation of Axes

A change of axes that transforms vectors through $F' = aF$ changes $F = fn$ to $aF = afa^{-1}an$ so that if $f' = afa^{-1}$ then $F' = f'n'$.

In order to relate the stress to other quantities through a matrix we wish to convert it into a single column matrix. We put $f_{11} = X_1$, $f_{22} = X_2$, $f_{33} = X_3$, $f_{23} = f_{32} = X_4$, $f_{31} = f_{13} = X_5$ and $f_{12} = f_{21} = X_6$.

Changing to the X representation we find

$$x' = \alpha X' \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8.1)$$

where α is the matrix eq. (7.2).

Strain Theory

If the dimensions of a body change, a point $p = \begin{pmatrix} p_1 \\ p_2 \\ p_3 \end{pmatrix}$ is moved to $p + \sigma_p$ where $\sigma_p = \begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \end{pmatrix}$. A neighboring point $p + u$ is moved by an amount σ_{p+u} given by $\sigma_{p+u} = (\nabla\sigma_c)_c u + \sigma_p$. The movement of $p + u$ relative to p is $\sigma = \sigma_{p+u} - \sigma_p = (\nabla\sigma_c)_c u$.

The 9 components of $(\nabla\sigma_c)_c$ describe the sort of movement in the neighborhood of a point; they are the strain coefficients. If the strain matrix is $\epsilon = (\nabla\sigma_c)_c$, a transformation $x' = ax$ causes this to become $a\epsilon a_c = (a\nabla\sigma_c a_c)_c$ and if $a\nabla = \nabla'$ and $a\sigma = \sigma'$ so that $\sigma_c a_c = \sigma_c'$ we have $\epsilon' = (\nabla'\sigma_c)_c$ if

$$\epsilon' = a\epsilon a_c \qquad (8.2)$$

When we arrange ϵ as a single column matrix e we shall, following custom, take $e_4 = \frac{\partial\sigma_2}{\partial x_3} + \frac{\partial\sigma_3}{\partial x_3}$, $e_5 =$ etc. This has the effect of moving the 2's of the α matrix to the conjugate position so that, while x transforms as $x' = \alpha x$, e transforms as $e' = \alpha_c^{-1} e$.

We shall take tensions as positive stress elements, and elongations as positive strain elements. The shear strain, $e_c = (0, 0, 0, 0, 0\ e_6)$ becomes upon rotating through 45° about x_3, $e_c' = \left(\frac{e_6}{2}, -\frac{e_6}{2}, 0, 0, 0, 0\right)$. This shows that to be consistent, a positive shear strain about x_3 must mean an expansion along the line $x_1 = x_2$ and an equal contraction along the line $x_1 = -x_2$.

A positive shear stress is one that tends to produce a positive shear strain.

By superposing such strain elements we see that the ϵ matrix (useful in displacement problems) may be formed from the e matrix (which is useful in stress strain relation) as

$$\epsilon = \begin{pmatrix} e_1, & \frac{1}{2}e_6 & \frac{1}{2}e_5 \\ \frac{1}{2}e_6 & e_2 & \frac{1}{2}e_4 \\ \frac{1}{2}e_5 & \frac{1}{2}e_4 & e_3 \end{pmatrix} \qquad (8.3)$$

This slightly awkward relation is used solely to make the "work done in straining" expressible as

$$2W = X_c e = e_c X \qquad (8.4)$$

If the e's were taken as equal to the ϵ's the work would be: $2W = X_1e_1 + X_2e_2 + X_3e_3 + 2X_4e_4 + 2X_5e_5 + 2X_6e_6$. This would be awkward in some later problems.

If the scalar W is to be unaffected by a transformation a we must have $W = e_c X$ unaffected. If we write

$$W = e_c \alpha^{-1} \alpha X = e_c \alpha^{-1} X'$$

we have

$$W' = W = e_c' X'$$

if

$$e_c' = e_c \alpha^{-1}$$

when

$$e' = \alpha_c^{-1} e_c \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8.5)$$

This substantiates our previous statement.

Relation Between Stress and Strain

If the strain in an elastic body is proportioned to the stress we may write:

$$e_1 = S_{11}X_1 + S_{12}X_2 + \cdots S_{16}X_6$$
$$e_2 = S_{21}X_1 + \cdots \qquad \cdots$$

Where the S's are elastic modulii. In matrix notation:

$$e = SX \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8.6)$$

Conversely $X = S^{-1}e$ or if $S^{-1} = C$

$$X = Ce \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8.7)$$

The C's are called elastic constants to distinguish them from the modulii S.

As $e = SX$, $\alpha_c^{-1} e = \alpha_c^{-1} S \alpha^{-1} \alpha X$, and since $\alpha_c^{-1} e = e'$, (the representation of e on a new axis system related to the old one through the matrix a) and αX is X', then we may write $(\alpha_c^{-1} e) = (\alpha_c^{-1} S \alpha^{-1})(\alpha X)$ as:

$$e' = S'X' \quad \text{where} \quad S' = \alpha_c^{-1} S \alpha^{-1} \quad \ldots\ldots\ldots\ldots (8.8)$$

Similarly operating on $X = Ce$ we find

$$X' = C'e' \quad \text{where} \quad C' = \alpha C \alpha_c \quad \ldots\ldots\ldots\ldots\ldots (8.9)$$

The energy required to cause the strain e is

$$W = \int X_r \, de_r = \frac{1}{2} X_r e_r = \frac{1}{2} S_{rs} X_r X_s \quad \ldots\ldots\ldots (8.10)$$

whence, if W is a perfect differential,

$$S_{rs} = \frac{\partial^2 W}{\partial X_r \, \partial X_s} = \frac{\partial^2 W}{\partial X_s \, \partial X_r} = S_{sr} \quad \ldots\ldots\ldots\ldots (8.11)$$

Similarly

$$C_{rs} = C_{sr} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8.12)$$

This reduces the constants and modulii to 21 of each.

If a transformation is performed that is permitted by the symmetry of the medium the elastic modulus matrix is unaltered. The monoclinic system has a binary axis. If we choose this as x_3 and rotate the axes 180° about this by means of the matrix $a = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$ we have $S' = \alpha_c^{-1} S \alpha^{-1} = S$.

$$\begin{pmatrix} 1&0&0 & 0 & 0&0 \\ 0&1&0 & 0 & 0&0 \\ 0&0&1 & 0 & 0&0 \\ 0&0&0 & -1 & 0&0 \\ 0&0&0 & 0 & -1&0 \\ 0&0&0 & 0 & 0&1 \end{pmatrix} \begin{pmatrix} S_{11}S_{12}S_{13}S_{14}S_{15}S_{16} \\ S_{12}S_{22}S_{23}S_{24}S_{25}S_{26} \\ S_{13}S_{23}S_{33}S_{34}S_{35}S_{36} \\ S_{14}S_{24}S_{34}S_{44}S_{45}S_{46} \\ S_{15}S_{25}S_{35}S_{45}S_{55}S_{56} \\ S_{16}S_{26}S_{36}S_{46}S_{56}S_{66} \end{pmatrix} \begin{pmatrix} 1&0&0 & 0 & 0&0 \\ 0&1&0 & 0 & 0&0 \\ 0&0&1 & 0 & 0&0 \\ 0&0&0 & -1 & 0&0 \\ 0&0&0 & 0 & -1&0 \\ 0&0&0 & 0 & 0&1 \end{pmatrix}$$

$$\begin{pmatrix} S_{11} & S_{12} & S_{13} & -S_{14} & -S_{15} & S_{16} \\ S_{12} & S_{22} & S_{23} & -S_{24} & -S_{25} & S_{26} \\ S_{13} & S_{23} & S_{33} & -S_{34} & -S_{35} & S_{36} \\ -S_{14} & -S_{24} & -S_{34} & S_{44} & S_{45} & -S_{46} \\ -S_{15} & -S_{25} & -S_{35} & S_{45} & S_{55} & -S_{56} \\ S_{16} & S_{26} & S_{36} & -S_{46} & -S_{56} & S_{66} \end{pmatrix}$$

Equating terms, those whose signs differ in S and S' must vanish.

Proceeding in this way through the 32 crystal classes we arrive at the ten following matrices that cover the elastic behaviour of all 32 classes.

Triclinic System
21 modulii

$$S = \begin{pmatrix} S_{11} & S_{12} & S_{13} & S_{14} & S_{15} & S_{16} \\ S_{12} & S_{22} & S_{23} & S_{24} & S_{25} & S_{26} \\ S_{13} & S_{23} & S_{33} & S_{34} & S_{35} & S_{36} \\ S_{14} & S_{24} & S_{34} & S_{44} & S_{45} & S_{46} \\ S_{15} & S_{25} & S_{45} & S_{45} & S_{55} & S_{56} \\ S_{16} & S_{26} & S_{36} & S_{46} & S_{56} & S_{66} \end{pmatrix}$$

The C matrix is entirely analogous

$\ldots\ldots\ldots\ldots\ldots (8.13)$

Monoclinic System
x_3 axis binary
13 modulii

$$S = \begin{pmatrix} S_{11} & S_{12} & S_{13} & 0 & 0 & S_{16} \\ S_{12} & S_{22} & S_{23} & 0 & 0 & S_{26} \\ S_{12} & S_{23} & S_{33} & 0 & 0 & S_{36} \\ 0 & 0 & 0 & S_{44} & S_{45} & 0 \\ 0 & 0 & 0 & S_{45} & S_{55} & 0 \\ S_{16} & S_{26} & S_{36} & 0 & 0 & S_{66} \end{pmatrix}$$

The C matrix is entirely analogous

$\ldots\ldots\ldots\ldots\ldots (8.14)$

Phombis System
x_3 binary
9 modulii

$$S = \begin{pmatrix} S_{11} & S_{12} & S_{13} & 0 & 0 & 0 \\ S_{12} & S_{22} & S_{23} & 0 & 0 & 0 \\ S_{23} & S_{23} & S_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & S_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & S_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & S_{66} \end{pmatrix}$$

The C matrix is entirely analogous

.....(8.15)

Tetragonal System
x_3 a fourfold axis
(Classes 9, 10, 13)
7 modulii

$$S = \begin{pmatrix} S_{11} & S_{12} & S_{13} & 0 & 0 & S_{16} \\ S_{12} & S_{11} & S_{13} & 0 & 0 & -S_{16} \\ S_{13} & S_{13} & S_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & S_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & S_{44} & 0 \\ S_{16} & -S_{16} & 0 & 0 & 0 & S_{66} \end{pmatrix}$$

The C matrix is entirely analogous

.....(8.16)

Tetragonal System
x_3 a fourfold axis
x_1 a twofold axis
(Classes 11, 12, 14, 15)
6 modulii

$$S = \begin{pmatrix} S_{11} & S_{12} & S_{13} & 0 & 0 & 0 \\ S_{12} & S_{11} & S_{13} & 0 & 0 & 0 \\ S_{13} & S_{13} & S_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & S_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & S_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & S_{66} \end{pmatrix}$$

The C matrix is entirely analogous

.....(8.17)

Trigonal System
x_3 trigonal axis
(Classes 16, 17)
7 modulii

$$S = \begin{pmatrix} S_{11} & S_{12} & S_{13} & S_{14} & -S_{15} & 0 \\ S_{12} & S_{11} & S_{13} & -S_{14} & S_{25} & 0 \\ S_{13} & S_{13} & S_{33} & 0 & 0 & 0 \\ S_{14} & -S_{14} & 0 & S_{44} & 0 & 2S_{25} \\ -S_{25} & S_{25} & 0 & 0 & S_{44} & 2S_{14} \\ 0 & 0 & 0 & 2S_{25} & 2S_{14} & 2(S_{11}-S_{12}) \end{pmatrix}$$

The C matrix is analogous except that
$C_{46} = C_{25}$
$C_{56} = C_{14}$
$C_{66} = \frac{1}{2}(C_{11} - C_{12})$

.....(8.18)

Trigonal System
x_3 trigonal axis
x_1 binary (Classes 18, 20, 21)
6 modulii
(alpha quartz)

$$S = \begin{pmatrix} S_{11} & S_{12} & S_{13} & S_{14} & 0 & 0 \\ S_{12} & S_{11} & S_{13} & -S_{14} & 0 & 0 \\ S_{13} & S_{13} & S_{33} & 0 & 0 & 0 \\ S_{14} & -S_{14} & 0 & S_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & S_{44} & 2S_{14} \\ 0 & 0 & 0 & 0 & 2S_{14} & 2(S_{11}-S_{12}) \end{pmatrix}$$

The C matrix is analogous except that
$C_{56} = C_{14}$
$C_{66} = \frac{1}{2}(C_{11} - C_{12})$

.....(8.19)

Hexagonal System
x_3 a sixfold axis
x_1 a twofold axis
(Classes 19, 22, 23, 24, 25, 26, 27)
5 modulii

$$S = \begin{pmatrix} S_{11} & S_{12} & S_{13} & 0 & 0 & 0 \\ S_{12} & S_{11} & S_{13} & 0 & 0 & 0 \\ S_{13} & S_{13} & S_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & S_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & S_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & 2(S_{11}-S_{12}) \end{pmatrix}$$

The C matrix is analogous except that
$C_{66} = \frac{1}{2}(C_{11} - C_{12})$

.....(8.20)

Cubic System
x_1, x_2 and x_3
fourfold axes
3 modulii

$$S = \begin{pmatrix} S_{11} & S_{12} & S_{12} & 0 & 0 & 0 \\ S_{12} & S_{11} & S_{12} & 0 & 0 & 0 \\ S_{12} & S_{12} & S_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & S_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & S_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & S_{44} \end{pmatrix}$$

The C matrix is entirely analogous

.....(8.21)

Isotropic bodies
2 modulii

$$S = \begin{pmatrix} S_{11} & S_{12} & S_{12} & 0 & 0 & 0 \\ S_{12} & S_{11} & S_{12} & 0 & 0 & 0 \\ S_{12} & S_{12} & S_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & S_2 & 0 & 0 \\ 0 & 0 & 0 & 0 & S_2 & 0 \\ 0 & 0 & 0 & 0 & 0 & S_2 \end{pmatrix}$$

$$S_2 = 2\,(S_{11} - S_{12})$$

The C matrix is analogous except that $C_2 = \frac{1}{2}\,(C_{11} - C_{12})$

.....(8.22)

Several Elastic Ratios in common use are given here for reference:

Young's Modulus: A tension stress X divided by the component of strain in the direction of X, $Y_i = \dfrac{X_i}{e_i}$. If the coordinate axes are chosen so that the stress lies along X_1, $Y_1 = \dfrac{1}{S_{11}}$. To find the value of Y in an arbitrary direction, (θ, φ) find S' for a transformation that puts X' in the direction (θ, φ)

$$S' = \alpha_c^{-1} S \alpha^{-1}$$

Where α is taken as form (21.4). Whence we obtain:

$$\begin{aligned} \left(\frac{1}{Y_{\theta,\varphi}}\right) = {} & c_1^4 s_2^4 S_{11} + s_1^4 s_2^4 S_{22} + c_2^4 S_{33} + s_1^2 s_2^2 c_2^2 S_{44} + c_1^2 c_2^2 s_2^2 S_{55} + c_1^2 s_1^2 s_2^4 S_{66} \\ & + 2c_1^2 s_1 c_2 s_2^3 S_{56} + 2c_1 s_1^2 c_2 s_2^3 S_{46} + 2c_1 s_1 c_2^2 s_2^2 S_{56} + 2c_1 s_1^3 s_2^4 S_{26} \\ & + 2c_1^3 s_1 s_2^4 S_{16} + 2c_1^3 s_2^3 c_1 S_{15} + 2c_1^2 s_1 s_2^3 c_2 S_{14} + 2c_1^2 c_2^2 s_2^2 S_{13} \\ & + 2c_1^2 s_1^2 s_2^4 S_{12} + 2s_1^2 c_2^2 s_2^2 S_{23} + 2s_1 s_2 c_2^3 S_{34} + 2c_1 s_1 c_2^2 s_2^2 S_{45} \\ & + 2c_1 c_2^3 s_2 S_{35} + 2c_1 s_1^2 c_2 s_2^3 S_{25} + 2s_1^3 c_2 s_2^3 S_{24} \end{aligned} \quad \text{.....(8.23)}$$

Rigidity Modulus: The shearing stress divided by the component of shear about the axis of shearing stress. For shear about x_1,

$$N_1 = \frac{1}{S_{44}} \quad \text{.....(8.24)}$$

Its value in another directions can be found as $Y_{\theta\varphi}$ was above.

The bulk modulus: The change in volume per unit volume for unit hydrostatic pressure is the bulk modulus, H. For a stress $X_c = (1, 1, 1, 0, 0, 0)$

$$e = (S_{11} + S_{12} + S_{31}, S_{12} + S_{33} + S_{23}, S_{31} + S_{23} + S_{33}, \cdots)$$

$$H = (\epsilon_1 + \epsilon_2 + \epsilon_3 = S_{11} + S_{22} + S_{33} + 2S_{12} + 2S_{31} + 2S_{23}) \quad (8.25)$$

This is obviously independent of the choice of axes.

The Temperature Coefficient of the Elastic Modulii and Constants

If

$$C = C^\circ + th + t^2h^1 + t^3h^2 + \cdots \quad (8.26)^*$$

and

$$S = S^\circ + th + t^2H^1 + t^3H^2 + \cdots \quad (8.27)$$

(C° and S° denote the values of the C's and S's for some standard temperature $t = 0$) then as the transformations are

$$C' = \alpha\, C\, \alpha_c \quad \text{and} \quad S' = \alpha_c^{-1} S \alpha^{-1} \quad \text{or}$$

$$C' = \alpha\, (C^\circ + th + t^2h^1 + t^3h^{1'} \cdots)\alpha_c$$

and

$$S' = \alpha_c^{-1}(S^\circ + tH + t^2H^1 + t^3H^1 \cdots)\, \alpha^{-1}$$

we see that

$$C' = C^{\circ 1} + th' + t^2h^{1'} \cdots \quad (8.28)$$

$$S' = S^{\circ 1} + tH' + t^2H^{1'} \cdots \quad (8.29)$$

where

$$h' = \alpha h \alpha_c \text{ etc.} \quad (8.30)$$

$$H' = \alpha_c^{-1} H \alpha^{-1} \text{ etc.} \quad (8.31)$$

That is, the h's transform as the C's do, and the H's transform as the S's do. Consequently we may copy their respective forms from the C and S matrices for any particular crystal class.

When the temperature coefficients of the constants or modulii are known in the form:

$$C_{ij} = C^\circ_{ij}\,(1 + tT_{c_{ij}}) \quad (8.32)$$

$$S_{ij} = S'_{ij}\,(1 + tT_{s_{ij}}) \quad (8.33)$$

* The n of t^n denotes the nth power of the scalar t; the n of h^n is merely another matrix, it does not mean a power.

we may write:

$$h_{ij} = C^{\circ}_{ij} T_{c_{ij}} \quad (8.34)$$

$$H_{ij} = S^{\circ}_{ij} T_{s_{ij}} \quad (8.35)$$

Multiplying (5) by (6) we get:

$$SC = I = S^{\circ}C^{\circ} = S^{\circ}C^{\circ} + t(S^{\circ}h + HC^{\circ}) + t^2(S^{\circ}h^1 + Hh + h^1C^{\circ}) + \cdots$$

whence, for this relation to hold for all values of t:

$$S^{\circ}h + HC^{\circ} = 0 \quad (8.36)$$

whence

$$\begin{aligned} h &= -C^{\circ}HC^{\circ} \\ H &= -S^{\circ}hS^{\circ} \end{aligned} \quad (8.37)$$

also

$$S^{\circ}h^1 + Hh + H^1C^{\circ} = 0 \quad (8.38)$$

so that

$$\begin{aligned} h^1 &= hS^{\circ}h - C^{\circ}H^1C^{\circ} \\ H^1 &= HC^{\circ}H - S^{\circ}h^1S^{\circ} \end{aligned} \quad (8.39)$$

From these we can compute the h's given the H's and vice versa.

SECTION 9

Temperature Expansion

The change in the dimensions of a crystal caused by a temperature change can be considered as a strain. The shift of the terminus of a vector l relative to its origin is given from the strain matrix ϵ by the equation $\Delta l = t\epsilon l$

Since ϵ is symmetric a proper choice of axes makes it possible to make the strain per degree a diagonal matrix,

$$\Delta l = tAl \quad \text{where} \quad A = \begin{pmatrix} A_1 & 0 & 0 \\ 0 & A_2 & 0 \\ 0 & 0 & A_3 \end{pmatrix} \quad (9.1)$$

As l and Δl both transform as vectors, a transformation a causes A to transform as

$$A' = aAa^{-1} \quad (9.2)$$

The elongation per unit length per degree in the direction (θ, Φ) is

$$\Delta l_{\theta\varphi} = \begin{pmatrix} \cos\theta\sin\varphi, & \sin\theta\sin\varphi, & \cos\varphi \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{pmatrix} \begin{pmatrix} A_1 & 0 & 0 \\ 0 & A_2 & 0 \\ 0 & 0 & A_3 \end{pmatrix} \begin{pmatrix} \cos\theta\sin\varphi & \cdot & \cdot \\ \sin\theta\sin\varphi & \cdot & \cdot \\ \cos = \varphi & \cdot & \cdot \end{pmatrix}$$

whence

$$\Delta l_{\theta\varphi} = A_1\cos^2\theta\sin^2\varphi + A_2\sin^2\theta\sin^2\varphi + A_3\cos^2\varphi \quad \ldots\ldots (9.3)$$

The strain can easily be extended to a function of t and t^2 as follows:

$$\Delta l = tAl + t^2Bl \quad \ldots\ldots (9.4)$$

Applying the prefactor a to both sides and putting the idemfactor in between A and l and between B and l in the form $I = a^{-1}a$ we have:

$$a\Delta l = t(aAa^{-1})al + t^2(aBa^{-1})al \quad \text{or}$$

$$\Delta l' = t\,A'l' + t^2B'l' \quad \text{where}$$

$$A' = aAa^{-1} \qquad B' = aBa^{-1} \quad \ldots\ldots (9.5)$$

SECTION 10

Temperature Variation of the Isothermal Elastic Modulii and Stress Variation of the Temperature Expansion Coefficients

We can write the isothermal elastic modulus matrix at temperature $\theta + t$ as

$$S^i = S^{io} + tH \quad \ldots\ldots (10.1)$$

and the coefficient of temperature expansion at constant stress X as

$$\bar{A} = \bar{A}^\circ + LX \quad \ldots\ldots (10.2)$$

Let us take a unit cube of crystal about the cycle indicated in the table; starting with the cube in the unstressed unstrained state at absolute temperature θ:

Operation	Change in Stress	Change in Strain	Temp.
Heat at zero stress	0	$t\bar{A}^\circ$	θ to $\theta + t$
Apply X isothermally	X	$(S^{io} + tH)X$	$\theta + t$
Cool at Const. X	0	$-t(\bar{A}^\circ + LX)$	$\theta + t$ to θ
Apply $-X$ isothermally	$-X$	$-S^{io}X$	θ

If we sum the strain changes in this cycle to zero we have

$$H = L$$

so that we may write

$$S = \bar{S} + tH \quad \text{(10.1)}$$

$$\bar{A} = \bar{A}^\circ + HX \quad \text{(10.3)}$$

This tells us that we may determine the temperature coefficients of the elastic modulii by measuring the effect of stress on the temperature expansion coefficients.

In a similar way we find that if the isothermal elastic constant matrix at temp. $\theta + t$ is:

$$C^i = C^{io} + th \quad \text{(10.4)}$$

then the relation between temperature and stress at constant strain e is

$$X = tB \quad \text{(10.5)}$$

where

$$B = B^o + he \quad \text{(10.6)}$$

The Difference between the Specific Heats at Constant Stress and Constant Strain

Writing for the specific heats at constant stress and at constant strain σ^p and σ^v, respectively, we can perform the following cycle:

Operation	Change in Stress	Change in Strain	Temperature	Work In	Heat Out	Entropy
Heat at zero stress..	—	$t\bar{A}^\circ$	θ to $\theta + t$	0	$-\rho t\sigma^p$	$\frac{-\rho t\sigma^p}{\theta + t/2}$
Restore zero strain isothermally	—	$-t\bar{A}^\circ$	$\theta + t$	$\frac{t^2}{2}\bar{A}_c^\circ C\bar{A}^\circ$	Q	$\frac{Q}{\theta + t}$
Cool at zero strain ..	—	0	$\theta + tt\sigma\theta$	0	$\rho t\sigma^v$	$\frac{\rho t\sigma^v}{\theta + \frac{t}{2}}$

Equating the sum of the entropy changes to zero:

$$Q = \left(1 + \frac{t}{2\theta} - \frac{t^2}{4\theta^2} \cdots\right) \rho t(\sigma^p - \sigma^v)$$

Equating the work in to the heat out:

$$(\sigma^p - \sigma^v) = \frac{\theta}{\rho}\bar{A}_c^\circ C\bar{A}^\circ \quad \text{(10.7)}$$

Isothermal and Adiabatic Elastic Modulii

Let us take a unit crystal cube at temperature θ, apply any stress X adiabatically, heat it to bring the temperature back to θ at constant stress then release it isothermally. The cycle is analyzed in the table:

Operation	Change in Stress	Change in Strain	Temperature	Work In	Heat Out	Entropy Change
Apply X adiabatically.....	X	S^aX	θ to $\theta - t$	$\frac{1}{2}X_cS^aX$	0	0
Heat to θ at const. X .	0	$t(\bar{A}^\circ + HX)$	$\theta - t$ to θ	$tX_c(\bar{A}^\circ + HX)$	$-t\rho\sigma^p$	$\frac{-t\rho\sigma^p}{\theta - t/2}$
Remove X isothermally	$-X$	$-S^{io}X$	θ	$-\frac{1}{2}X_cS^{io}X$	Q	Q/θ

Summing the strains to zero:

$$(S^{io} - S^a)X = t(\bar{A}^\circ + HX)$$

If we equate the total entropy change to zero we obtain an expression for Q that can be substituted in the relation "work in = Heat out." This gives us:

$$-\tfrac{1}{2}X_c(S^{io} - S^a)X + tX(\bar{A}^\circ + HX) = \tfrac{1}{2}\frac{t^2\rho\sigma^p}{\theta}$$

and from these two expressions we derive, writing ϕ for $S^{io} - S^a$:

$$\phi = \frac{\theta}{\rho\sigma^p}(\bar{A}^\circ + HX)(\bar{A}^\circ + HX)_c \quad \ldots\ldots\ldots\ldots (10.8)$$

which is, to the first order of the small quantities X:

$$\phi = \frac{\theta}{\rho\sigma^p}\bar{A}^\circ\bar{A}^\circ_c + 2HX\bar{A}^\circ_c \quad \ldots\ldots\ldots\ldots\ldots (10.9)$$

and since $X = C\epsilon$ we have also

$$\frac{\theta}{\rho\sigma P}(\bar{A}^\circ + 2HCe)\bar{A}^\circ \quad \ldots\ldots\ldots\ldots\ldots (10.10)$$

Whence we see that as the stress approaches zero as a limit ϕ approaches $\phi^\circ = \frac{\theta}{\rho\sigma^p}\bar{A}^\circ\bar{A}^\circ_c$. If we write similarly $C^{io} - C^a = \psi$ we have multiplying $S^{io} = S^a + \phi$ by $C^{io} = C^a + \psi$ and dropping higher orders of small quantities:

$$\psi = -C^{io}\phi C^{io} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (10.11)$$

For example we have for quartz at 20° Centigrade

$$\phi^\circ = \frac{293 \times 10^{-12}}{2.65 \times 7.37 \times 10^6} \begin{pmatrix} 14.4 \\ 14.4 \\ 7.8 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} (14.4 \;\; 14.4 \;\; 7.8 \;\; 0 \;\; -0 \;\; 0)$$

$$= \begin{pmatrix} 3.13 & 3.13 & 1.69 & 0 & 0 & 0 \\ 3.13 & 3.13 & 1.69 & 0 & 0 & 0 \\ 1.69 & 1.69 & .907 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} 10^{-15} \quad \text{and as}$$

$$S^{io} = 10^{-15} \times \begin{pmatrix} 1298 & -166 & -152 & -431 & 0 & 0 \\ -166 & 1298 & -152 & 431 & 0 & 0 \\ -152 & -152 & 990 & 0 & 0 & 0 \\ -431 & 431 & 0 & 2005 & 0 & 0 \\ 0 & 0 & 0 & 0 & 2005 & 862 \\ 0 & 0 & 0 & 0 & 862 & 2928 \end{pmatrix}$$

whence $\phi_{11} = S^{io}_{11}\ (1 - .00241)$

$\phi_{12} = S^{io}_{12}\ (1 - .0189)$

$\phi_{13} = S^{io}_{13}\ (1 - .0111)$

$\phi_{33} = S^{io}_{33}\ (1 - .000917)$

For Rochelle Salt we have:

$$\phi = \frac{293 \times 10^{-12}}{1.79 \times 15.5 \times 10^6} \begin{pmatrix} 59.9 \\ 38.1 \\ 44.8 \\ 4 \\ 0 \\ 0 \end{pmatrix} (59.9 \;\; 38.1 \;\; 44.8 \;\; 0 \;\; 0 \;\; 0)$$

$$= \begin{pmatrix} 38.0 & 24.2 & 28.5 & 0 & 0 & 0 \\ 24.2 & 15.4 & 18.1 & 0 & 0 & 0 \\ 28.5 & 18.1 & 21.3 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \times 10^{-15}$$

$$\text{As } S^{io} = \begin{pmatrix} 4690 & -795 & -2180 & 0 & 0 & 0 \\ -795 & 3205 & 1691 & 0 & 0 & 0 \\ -2180 & 1691 & 2815 & 0 & 0 & 0 \\ 0 & 0 & 0 & 6060 & 0 & 0 \\ 0 & 0 & 0 & 0 & 3060 & 0 \\ 0 & 0 & 0 & 0 & 0 & 8020 \end{pmatrix} \times 10^{-15}$$

So that

$$\phi_{11} = S^{io}_{11}\ (1 - .0080) \qquad \phi_{12} = S^{io}_{12}\ (1 - .0305)$$

$$\phi_{22} = S^{io}_{22}\ (1 - .0050) \qquad \phi_{13} = S^{io}_{13}\ (1 - .0103)$$

$$\phi_{33} = S^{io}_{33}\ (1 - .0076) \qquad \phi_{23} = S^{io}_{23}\ (1 - .0107)$$

$$\phi_{44} = S^{io}_{44}$$

$$\phi_{55} = S^{io}_{55}$$

$$\phi_{66} = S^{io}_{66}$$

At the temperature of maximum piezo activity the components of ϕ for Rochelle are smaller by about $3\frac{1}{2}\%$.

SECTION 11

The Piezo-electric Effect

Some crystals develop an electric charge when subjected to mechanical stresses. As far as the effect is linear it may be expressed by:

$$\begin{aligned} D_1 &= d_{11}X_1 + d_{12}X_2 \cdots d_{16}X_6 \\ D_2 &= d_{21}X_1 + \cdots \\ D_3 &= d_{31}X_1 + \cdots \qquad d_{36}X_6 \end{aligned} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (11.1)$$

or in matrix notation

$$D = dX \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (11.2)$$

where the 18 constants d_{ij} are called piezo-electric constants, and D is the electric induction.

On rotating the axes by means of a transformation a, the vector D becomes D' where $D' = aD$. The stress transforms as $X' = \alpha X$ whence $D = dX$ becomes $D' = ad\alpha^{-1}X'$ or $D' = d'X'$ where:

$$d' = ad\alpha^{-1} \cdots \ldots\ldots\ldots\ldots\ldots\ldots\ldots (11.3)$$

If transformations permitted by symmetry are performed, the d matrix is unchanged. Class 3 has a binary axis only, if we choose this as x_3 and perform the transformation

$$a = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \text{we find:}$$

$$d = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

$$d = \begin{pmatrix} -d_{11} & -d_{12} & -d_{13} & d_{14} & d_{15} & -d_{16} \\ -d_{21} & -d_{22} & -d_{23} & d_{24} & d_{25} & -d_{26} \\ d_{31} & d_{32} & d_{33} & -d_{34} & -d_{35} & d_{36} \end{pmatrix}$$

For this to be consistent with the original d matrix the terms with conflicting signs must vanish.

Applying similar analyses to each of the 32 classes we arrive at the set of matrices:

Class 1 (asymmetric)
No symmetry

$$d = \begin{pmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{pmatrix} \quad (11.01)$$

Class 2 (triclinic pinacoidal), center of symmetry $d = 0$ . . . . . (11.02)

Class 3 (monoclinic sphenoidal
x_3 is binary

$$d = \begin{pmatrix} 0 & 0 & 0 & d_{14} & d_{15} & 0 \\ 0 & 0 & 0 & d_{24} & d_{25} & 0 \\ d_{31} & d_{32} & d_{33} & 0 & 0 & d_{36} \end{pmatrix} \quad \begin{matrix} \text{(sucrose)} \\ (11.03) \end{matrix}$$

Class 4 (monoclinic domatic)
x_3 plane is plane of
symmetry

$$d = \begin{pmatrix} d_{11} & d_{12} & d_{13} & 0 & 0 & d_{16} \\ d_{21} & d_{22} & d_{23} & 0 & 0 & d_{26} \\ 0 & 0 & 0 & d_{34} & d_{35} & 0 \end{pmatrix} \quad (11.04)$$

Class 5 (monoclinic prismatic) center of symmetry, $d = 0$ . . . . . (11.05)

Class 6 (Orthorhombic
bisphenoidal)
x_1, x_2, x_3 binary

$$d = \begin{pmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{25} & 0 \\ 0 & 0 & 0 & 0 & 0 & d_{36} \end{pmatrix} \quad \begin{matrix} \text{(Rochelle)} \\ (11.06) \end{matrix}$$

Class 7 (Orthorhombic
Pyramidal)
x_3 binary, x_1 and x_2
planes of symmetry

$$d = \begin{pmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{24} & 0 & 0 \\ d_{31} & d_{32} & d_{33} & 0 & 0 & 0 \end{pmatrix} \quad (11.07)$$

Class 8 (Orthorhombic bipyramidal), center of symmetry, $d = 0$ (11.08)

Class 9 (Tetragonal bisphenoidal) x_3 is quaternary alternating

$$d = \begin{pmatrix} 0 & 0 & 0 & d_{14} & d_{15} & 0 \\ 0 & 0 & 0 & -d_{15} & d_{14} & 0 \\ d_{31} & -d_{31} & 0 & 0 & 0 & d_{36} \end{pmatrix} \quad (11.09)$$

Class 10 (Tetragonal pyramidal) x_3 is quaternary

$$d = \begin{pmatrix} 0 & 0 & 0 & d_{14} & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & -d_{14} & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix} \quad (11.10)$$

Class 11 (Tetragonal scalenohedral) x_3 quaternary, x_1 and x_2 binary

$$d = \begin{pmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & d_{36} \end{pmatrix} \quad (11.11)$$

Class 12 (Tetragonal trapezohedral) x_3 quaternary, x_1 and x_2 binary

$$d = \begin{pmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -d_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad (11.12)$$

Class 13 (Tetragonal bipyramidal) center of symmetry, $d = 0$ (11.13)

Class 14 (Ditetragonal pyramidal) x_3 quaternary x_1 and x_2 planes of symmetry

$$d = \begin{pmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix} \quad (11.14)$$

Class 15 (Ditetragonal bipyramidal) center of symmetry, $d = 0$ (11.15)

Class 16 (Trinonal pyramidal) x_3 trigonal

$$d = \begin{pmatrix} d_{11} & -d_{11} & 0 & d_{14} & d_{15} & -2d_{22} \\ -d_{22} & d_{22} & 0 & d_{15} & -d_{14} & -2d_{11} \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix} \quad (11.16)$$

Class 17 (Trigonal rhombohedral) center of symmetry, $d = 0$ (11.17)

Class 18 (Trigonal) (Quartz) trapezohedral) x_3 trigonal, x_1 binary

$$d = \begin{pmatrix} d_{11} & -d_{11} & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -d_{14} & -2d_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad (11.18)$$

Class 19 (Trigonal bipyramidal) x_3 trigonal, x_3 plane of symmetry

$$d = \begin{pmatrix} d_{11} & -d_{11} & 0 & 0 & 0 & -2d_{22} \\ -d_{22} & d_{22} & 0 & 0 & 0 & -2d_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad (11.19)$$

Class 20 (Ditrigonal pyramidal) x_3 trigonal, x_2 plane of symmetry

$$d = \begin{pmatrix} 0 & 0 & 0 & 0 & d_{15} & -2d_{22} \\ -d_{22} & d_{22} & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix} \quad \begin{matrix} \text{(tourma-} \\ \text{line)} \\ (11.20) \end{matrix}$$

Class 21 (Ditrigonal scalenohedral) center of symmetry, $d = 0$ (11.21)

Class 22 (Ditrigonal bipyramidal)
x_3 trigonal, x_3 plane of symmetry
x_2 plane of symmetry

$$d = \begin{pmatrix} d_{11} & -d_{11} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -2d_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \tag{11.22}$$

Class 23 (Hexagonal pyramidal)
x_3 Hexagonal

$$d = \begin{pmatrix} 0 & 0 & 0 & d_{14} & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & -d_{14} & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix} \tag{11.23}$$

Class 24 (Hexagonal trapezohedral)
x_3 hexagonal, x_1 binary

$$d = \begin{pmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -d_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \tag{11.24}$$

Class 25 (Hexagonal bipyramidal) center of symmetry, $d = 0$ (11.25)

Class 26 (Dihexagonal pyramidal)
x_3 hexagonal, x_2 plane

$$d = \begin{pmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix} \tag{11.26}$$

Class 27 (Dihexagonal bipyramidal) center of symmetry, $d = 0$ (11.27)

Class 28 (Cubic tetrahedral-pentagonal-dedocahedral)
x_1, x_2, x_3 binary

$$d = \begin{pmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & d_{14} \end{pmatrix} \tag{11.28}$$

Class 29 (Cubic pentagonal-icositetrahedral) $d = 0$ (11.29)

Class 30 (Cubic, dyakisdodecahedral) center of symmetry, $d = 0$ (11.30)

Class 31 (Cubic, hexakis-tetrahedral)
x_1, x_2, x_3 quaternary alternating

$$d = \begin{pmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & d_{14} \end{pmatrix} \tag{11.31}$$

Class 32 (Cubic, hexakis-octahedral) center of symmetry, $d = 0$ (11.32)

Whenever a center of symmetry exists the piezo-electric property vanishes since a center of symmetry requires $d' = (-I)\, dI = -d = -d'$. Also $d = 0$ for the pentagonal icositetrahedral class.

Classes 6, 11, 12, 24, 28 and 31 polarize only by shear.

Classes 1, 3, 4, 7, 10, 14, 16, 20, 23, 26 can be polarized by hydrostatic pressure. As an example of this let us consider tourmaline (which is ditrigonal pyramidal). For hydrostatic pressure, $X_1 = X_2 = X_3$, $X_4 = X_5 = X_6 = 0$, whence from the polarization stress matrices we find, $D_1 = 0$, $D_2 = 0$, $D_3 = (2d_{31} + d_{23}) \times$ pressure. As $d_{31} = 0.75 \times 10^{-8}$ and $d_{33} = 5.8 \times 10^{-8}$ for tourmaline, we get 7.3 abcoulomlos per cm^2 per dyne per cm^2.

SECTION 12

The Converse Piezo-electric Effect

A stress X causes an electric induction

$$D = dX \quad \text{.....(11.2)}$$

and a strain

$$e = SX \quad \text{.....(8.7)}$$

If the charge is allowed to leak away a further strain occurs, at constant stress. This is the strain that would be gotten if the stress were originally applied with surfaces rendered conducting:

$$e^\circ = S^\circ X \quad \text{.....(12.1)}$$

In the first sort of stress, the work per unit volume done on the crystal by establishing the stress X is:

$$W = \tfrac{1}{2}X_c e = \tfrac{1}{2}X_c SX \quad \text{.....(8.4)}$$

The energy stored electrically in the medium is:

$$W_E = 2\pi D_c k^{-1} D \quad \text{.....(12.2)}$$

while the work done on a conducting crystal is:

$$W^\circ = \tfrac{1}{2}X_c S^\circ X \quad \text{.....(12.3)}$$

If a crystal be stressed in its insulated state by expenditure of energy W, the charges then absorbed by an external circuit taking up energy W_E, the strain changes from e to e° at constant stress so that the stresses perform additional work

$$W_a = X_c(e^\circ - e) = X_c(S^\circ - S)X$$

and the crystal is left containing energy W°. Whence

$$W^\circ = W - W_E + W_a \quad \text{.....(12.4)}$$

or:

$$\tfrac{1}{2}X_c S^\circ X = \tfrac{1}{2}X_c SX - 2\pi D_c k^{-1} D + X_c(S^\circ - S)X$$

so that:

$$X_c(S^\circ - S)X = 4\pi D_c k^{-1} D$$

If we substitute $D = dX$ we find

$$X_c(S^\circ - S)X = 4\pi X_c d_c k^{-1} dX$$

so that:

$$S^\circ - S = 4\pi d_c k^{-1} d \quad \ldots\ldots\ldots\ldots\ldots\ldots (12.5)$$

The change in strain caused by rendering the surfaces conducting is:

$$e^\circ - e = (S^\circ - S)X = 4\pi d_c k^{-1} dX \quad \ldots\ldots\ldots\ldots (12.6)$$

If the crystal be now insulated and the stress removed, an induction of opposite sign will occur and because of the assumed linear dependence of D on X the new induction will be equal to the negative of the previous one. The induction $D = -dX$ indicates an electric field:

$$E = 4\pi k^{-1} D = 4\pi k^{-1} dX \quad \ldots\ldots\ldots\ldots\ldots\ldots (12.7)$$

Also, the strain will alter by an amount $-e''$, where, since the action takes place with non-conducting surfaces:

$$e'' = SX$$

This leaves a strain on the crystal, of amount:

$$e' = e^\circ - e'' = (S^\circ - S)X \quad \ldots\ldots\ldots\ldots\ldots\ldots (12.8)$$

From (12.6), (12.7) and (12.8) it follows that:

$$e' = d_c E \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (12.9)$$

As the medium is in just the condition that an electric field E would put the unstressed medium, (12.9) is the equation of the converse piezo-electric effect. It is to be noted that the set of constants that relates polarization and stress is the conjugate of the set that relates electric field and strain. For convenience in notation the converse effect will be written as

$$e = gE \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (12.10)$$

where

$$g = d_c \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (12.11)$$

Rewriting (13) as $\alpha_c^{-1} e = (\alpha_c^{-1} g a^{-1}) a E$ we see that

$$e' = g' E'$$

where

$$g' = \alpha_c^{-1} g a \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (12.12)$$

SECTION 13

The Converse Piezo-electric Effect as a Non-Linear Function

If the strain of a crystal is not strictly a linear function of the electric field causing it we must relate the components of strain to field terms of the second power as well as to first power terms. That is, the equation $e = gE$ (which gives the strain e in terms of the electric field E through the 18 constants g) must be modified to include terms E_iE_j. All such terms are included in the symmetric matrix $(E\,E_c)$.

A transformation a that replaces E by a_cE' also replaces E_c by E'_ca so that $(E\,E_c)$ is replaced by $(a_cE'E'_ca)$, that is $(E\,E_c)$ being self-conjugate, transforms similarly to the stress matrix. We may rearrange this as a one column matrix similar to the stress matrix X, as follows:

$$(E\,E_c) = \begin{pmatrix} E_1^2 \\ E_2^2 \\ E_3^2 \\ E_2E_3 \\ E_3E_1 \\ E_1E_2 \end{pmatrix} = \overline{E} \quad \ldots\ldots\ldots\ldots\ldots\ldots (13.1)$$

We may now relate the strain to E and $\overline{E}$ through the two matrices g and G:

$$e = gE + G\overline{E} \quad \ldots\ldots\ldots\ldots\ldots\ldots (13.2)$$

If transformations permitted by the symmetry of the crystal are performed, g' must equal g and G' must equal G, this allows us to simplify the matrices; g is no different than before and hence vanishes for all types having centers of symmetry (and for the pentagonal icositetrahedral class).

Rewriting (1) as $\alpha_c^{-1}e = (\alpha_c^{-1}ga^{-1})aE + \alpha_c^{-1}Ga^{-1}aE$ we see that

$$e' = g'E' + G'\overline{E}$$

where

$$g' = \alpha_c^{-1}ga$$

$$G' = \alpha_c^{-1}G\alpha^{-1} \quad \ldots\ldots\ldots\ldots\ldots\ldots (13.3)$$

The matrix G transforms as the elastic modulii matrix does but $G_{ij} \neq G_{ji}$. Applying $G' = \alpha_cG\alpha$ we arrive at the set of matrices that follow

Triclinic (36 consts)

$$\begin{pmatrix} G_{11} & G_{12} & G_{13} & G_{14} & G_{15} & G_{16} \\ G_{21} & G_{22} & G_{23} & G_{24} & G_{25} & G_{26} \\ G_{31} & G_{32} & G_{33} & G_{34} & G_{35} & G_{36} \\ G_{41} & G_{42} & G_{43} & G_{44} & G_{45} & G_{46} \\ G_{51} & G_{52} & G_{53} & G_{54} & G_{55} & G_{56} \\ G_{61} & G_{62} & G_{63} & G_{64} & G_{65} & G_{66} \end{pmatrix} \tag{13.4}$$

Monoclinic (20 consts)

$$\begin{pmatrix} G_{11} & G_{12} & G_{13} & 0 & 0 & G_{13} \\ G_{21} & G_{22} & G_{23} & 0 & 0 & G_{26} \\ G_{31} & G_{32} & G_{33} & 0 & 0 & G_{36} \\ 0 & 0 & 0 & G_{44} & G_{45} & 0 \\ 0 & 0 & 0 & G_{54} & G_{55} & 0 \\ G_{61} & G_{62} & G_{63} & 0 & 0 & G_{66} \end{pmatrix} \tag{13.5}$$

Orthorhombic (12 consts)

$$\begin{pmatrix} G_{11} & G_{12} & G_{13} & 0 & 0 & 0 \\ G_{21} & G_{22} & G_{23} & 0 & 0 & 0 \\ G_{31} & G_{32} & G_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & G_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & G_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & G_{66} \end{pmatrix} \tag{13.6}$$

Tetragonal Classes 9, 10, 13) (10 consts)

$$\begin{pmatrix} G_{11} & G_{12} & G_{13} & 0 & 0 & G_{16} \\ G_{12} & G_{11} & G_{13} & 0 & 0 & -G_{16} \\ G_{31} & G_{31} & G_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & G_{44} & G_{45} & 0 \\ 0 & 0 & 0 & -G_{45} & G_{44} & 0 \\ G_{61} & -G_{61} & 0 & 0 & 0 & G_{66} \end{pmatrix} \tag{13.7}$$

Tetragonal Classes 11, 12, 14, 15) (7 consts)

$$\begin{pmatrix} G_{11} & G_{12} & G_{13} & 0 & 0 & 0 \\ G_{12} & G_{11} & G_{13} & 0 & 0 & 0 \\ G_{31} & G_{31} & G_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & G_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & G_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & G_{66} \end{pmatrix} \tag{13.8}$$

Trigonal (Classes 16, 17) (10 consts)

$$\begin{pmatrix} G_{11} & G_{12} & G_{13} & G_{14} & -G_{25} & 0 \\ G_{12} & G_{11} & G_{13} & -G_{14} & G_{25} & 0 \\ G_{31} & G_{31} & G_{33} & 0 & 0 & 0 \\ G_{41} & -G_{41} & 0 & G_{44} & G_{45} & 2G_{52} \\ -G_{52} & G_{52} & 0 & -G_{45} & G_{44} & 2G_{41} \\ 0 & 0 & 0 & 2G_{25} & 2G_{14} & 2(G_{11}-G_{22}) \end{pmatrix} \tag{13.9}$$

Trigonal (Classes 18, 20, 21) (8 constants)

$$\begin{pmatrix} G_{11} & G_{12} & G_{13} & G_{14} & 0 & 0 \\ G_{12} & G_{11} & G_{13} & -G_{14} & 0 & 0 \\ G_{31} & G_{31} & G_{33} & 0 & 0 & 0 \\ G_{41} & -G_{41} & 0 & G_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & G_{44} & 2G_{41} \\ 0 & 0 & 0 & 0 & 2G_{14} & 2(G_{11} - G_{12}) \end{pmatrix} \tag{13.10}$$

Trigonal (Classes 19, 22) (6 constants) Also Hexagonal (Classes 23, 24, 25, 26, 27)

$$\begin{pmatrix} G_{11} & G_{12} & G_{13} & 0 & 0 & 0 \\ G_{12} & G_{11} & G_{13} & 0 & 0 & 0 \\ G_{31} & G_{31} & G_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & G_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & G_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & 2(G_{11} - G_{12}) \end{pmatrix} \tag{13.11}$$

Cubic (Classes 28, 29, 30, 31 and 32) (5 Constants)

$$\begin{pmatrix} G_{11} & G_{12} & G_{12} & 0 & 0 & 0 \\ G_{12} & G_{11} & G_{12} & 0 & 0 & 0 \\ G_{12} & G_{12} & G_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & G_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & G_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & G_{44} \end{pmatrix} \quad (13.12)$$

Isotropic Bodies (2 Constants)

$$\begin{pmatrix} G_{11} & G_{12} & G_{12} & 0 & 0 & 0 \\ G_{12} & G_{11} & G_{12} & 0 & 0 & 0 \\ G_{12} & G_{12} & G_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & G & 0 & 0 \\ 0 & 0 & 0 & 0 & G & 0 \\ 0 & 0 & 0 & 0 & 0 & G \end{pmatrix} \quad (13.13)$$

$$G = 2(G_{11} - G_{12})$$

According to this analysis, all bodies suffer a change in dimensions when subjected to an electric field. These strains resulting from a field are generally much smaller than those strains $e = gE$ present only in crystals lacking a center of symmetry. For example, quartz has a strain of about 6.5×10^{-8} *cms/cm/ab* volt. Glass in a field of 1000 practical volts per cm has a strain of about 4×10^{-12}, in a 100,000 volt field it has 4×10^{-8}. Rubber in the 1000 volt field strains by about 7×10^{-8} and in the 100,000 volt field by about 7×10^{-4}. The 1st order quartz strain in these fields would be about 2.2×10^{-7} and 2.2×10^{-5} respectively.

The Second Order Piezo-electric Effect

If the induction stress relation is not strictly linear one can assume the induction to depend also on second order terms of the stress:

$$D = dX + p\,(\overline{XX_c})$$

where $(\overline{XX_c})$ is a single column matrix formed from the 21 elements of XX_c and p is a matrix of the 63 elements $p_{11,1} \ldots p_{33,3}$.

Since X transforms as $X' = \alpha X'$, (XX_c) transforms as $X'X_c' = \alpha XX_c\alpha_c$. In the same way that α was formed from a we can form a matrix $\bar{\alpha}$ that transforms the single column matrix $(\overline{XX_c})$ through $(\overline{XX_c})' = \bar{\alpha}(\overline{XX_c})'$.

$$aD = ad\alpha^{-1}\,X + ap(\bar{\alpha})^{-1}\,\bar{\alpha}(\overline{XX_c}) \text{ or}$$

$$D' = d'X' + p'(\overline{XX_c})'$$

where

$$d' = ad\alpha^{-1} \quad \text{and} \quad p' = ap(\bar{\alpha})^{-1}$$

The first order effect is the same as before. With the relation $p' = ap(\bar{\alpha})^{-1}$ we could perform the operations of symmetry permitted by the 32 crystal classes and obtain the reduced matrices. However since $\bar{\alpha}$ has 484 elements we shall limit ourselves to crystals with centers of symmetry.

As X is unchanged by an inversion through the origin, α is the idemfactor for this transformation and a is $-I$, also $(\bar{\alpha}) = I$. Therefore $D' = -D = D$ so that D vanishes.

It is to be noted that although there is a sort of reciprocity between the first order piezo effect and the converse effect, in that the matrices for one are the conjugates of the matrices of the other, there is no such reciprocity in the second order effects: if a center of symmetry exists no polarization can be brought about by stress either as a first order effect or as a second order effect; if a center of symmetry exists an electric field can cause a strain through the second order effect but not through the first order effect.

Dielectric Constants at Constant Stress and at Constant Strain

Let us consider a unit crystal cube, initially unstressed, unstrained and in zero electric field. We write k^p and k^v for the dielectric constant matrices at constant stress and constant strain, respectively, C^E as the elastic constant matrix at constant electric field E, C^o as the same for zero field. We study a cycle consisting of a strain caused by application of an electric field E at zero stress followed by a stress applied at constant E to reduce the strain to zero and completed by conducting away the electric charges at zero strain so that the body is left in its original state. The cycle is described by the table:

Operation	Change in Stress	Change in Strain	Change in Displacement Current	Change in Field	Energy Put In
Apply E	0	$d_c E$	$\frac{1}{4\pi} k^p E$	$E\frac{1}{8\pi}$	$E_c k^p E$
Apply $-\epsilon$....	$-C^E d_c E$	$-d_c E$	$-\frac{1}{4\pi}(k^p - k^v)E$	$0\frac{1}{2}$	$E_c d\, C^E d_c E -$
				$\frac{1}{4\pi}$	$E_c(k^p - k^v)E$
Apply $-E$ ...	$Cd_c E$	0	$-\frac{1}{4\pi} k^v E$	$-E - \frac{1}{8\pi}$	$E_c k^v E$

whence $C = C^E$; also

$$k^p - k^v = 4\pi\, dCd_c \ldots\ldots\ldots\ldots\ldots\ldots (13.14)$$

SECTION 14

Pyro-Electricity

If the electric polarization brought about by heating some kinds of crystals is simply a function of the uniform temperature change, that is if this polarization can be produced by taking the whole body quickly from the

uniform temperature $\underline{t}_0$ to the uniform temperature $\underline{t}_0 + \underline{t}$ the pyro-electric effect could be described by the equation:

$$\begin{pmatrix} D_1 \\ D_2 \\ D_3 \end{pmatrix} = \underline{t} \begin{pmatrix} \rho_1 \\ \rho_2 \\ \rho_3 \end{pmatrix} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (14.1)$$

where ρ is the pyro-electric matrix.

This can be approached in another way by considering the polarization as due to the uniform strain. We may hence write, since $X = Ce$: (i.e . stress matrix = elastic constant matrix times the strain matrix)

$$P = dX = dCe$$

where e is the strain brought about by the temperature change t. If $A = \begin{pmatrix} A_1 & 0 & 0 \\ 0 & A_2 & 0 \\ 0 & 0 & A_3 \end{pmatrix}$ is the temperature expansion matrix we have:

$$P = \underline{t}\, dC \begin{pmatrix} A_1 \\ A_2 \\ A_3 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

Now since d has 3 rows and the A matrix has but one column the product $dC\bar{A}$ has 3 rows and one column so that we may define ρ as $dC\bar{A}$.

As D of $D = t\rho$ transforms by $D' = aD$, so does ρ:

$$\rho' = a\rho$$

When a center of symmetry exists a permitted transformation is $a = -I$, whence $\rho = -\rho' = -\rho$ so that $\rho = 0$. No pyro-electric effect (on this theory) could exist for a crystal with a center of symmetry.

If a binary axis exists and is chosen as x_3 we have

$$\begin{pmatrix} \rho_1 \\ \rho_2 \\ \rho_3 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \rho_1 \\ \rho_2 \\ \rho_3 \end{pmatrix} = \begin{pmatrix} -\rho_1 \\ -\rho_2 \\ \rho_3 \end{pmatrix}$$

whence for this case

$$\rho = \begin{pmatrix} 0 \\ 0 \\ \rho_3 \end{pmatrix} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (14.2)$$

If another binary axis exists at right angles to this one we find $\rho = 0$.

This is seen seriously to limit the number of classes showing this kind of pyro-electric effect. In fact we find $\rho = 0$ for classes 2, 5, 6, 8, 9, 11, 12, 13, 15, 17, 18, 19, 21, 22, 24, 25, 27, 28, 29, 30, 31 and 32. The expression $\rho = \begin{pmatrix} 0 \\ 0 \\ \rho_3 \end{pmatrix}$ describes the pyro-electric effect in the classes, 3, 7, 10, 14, 16, 20, 23 and 26, while the expression $\rho = \begin{pmatrix} \rho_1 \\ \rho_2 \\ 0 \end{pmatrix}$ describes class 4, and only class 1 is described by

$$\rho = \begin{pmatrix} \rho_1 \\ \rho_2 \\ \rho_3 \end{pmatrix} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (14.3)$$

It is to be noted then that this theory excludes many classes ordinarily described as pyro-electric, such crystals as quartz in Class 18 for example. Consequently it would seem that whether or not this effect exists we must seek elsewhere for the explanation of the effect in quartz.

The effect can easily be explained as due to non-uniform temperature, which causes stress which in turn give rise to electric phenomena in piezo active crystals. For example a suddenly chilled crystal has its outer layers in a state of tension. This would produce just the pattern of positive and negative charges that one actually observes. As to whether the first effect exists, much argument between Lord Kelvin and others seems to have left the question still uncertain.

In pyro-electric crystals we would expect to find a difference in the piezo constants measured isothermally or adiabatically. If a temperature change t causes an electric displacement $D = \rho t$ the application of an electric field E should cause a temperature change t given by a relation such as:

$$t = \varphi E \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (14.4)$$

Also the temperature coefficient of expansion, A_s (for a crystal with faces rendered conducting) would differ from the coefficient A_i (for a crystal with an insulated surface).

If a crystal at temperature t_0 has suddenly applied to it a field E the temperature rises to $t_0 + \varphi E$ and the crystal strains, because of the converse piezo effect, by amount $\epsilon = g_a E$ where g_a is the adiabatic converse piezo matrix. If the field is now removed isothermally a further strain $g_i E$ takes place. If the faces are short-circuited and the temperature restored to t_0 a further strain $A_s t = A_s \varphi E$ takes place and the crystal is then in its

initial state. Equating the sum of the strains to zero we find $(g_a - g_i)$ $E = A_s\varphi E$ or

$$g_a - g_i = A_s\varphi \quad \ldots\ldots\ldots\ldots\ldots\ldots (14.5)$$

Let the initial state of a crystal be, temperature $= t_0$, stress, strain and field $= 0$. If the (electrically insulated) crystal is heated by amount t, a strain $A_i t$ is caused and also an electric displacement $D = \rho t$. There now exists an electric field $E = r\pi k^{-1}\rho t$. Let this field be discharged at constant temperature, giving a further strain of $g_i E = 4\pi g_i k^{-1}\rho t$. The crystal is now short-circuited and if the initial temperature is restored a strain $-A_s t$ follows. The crystal is now in its initial state. If we equate the sum of the strains to zero we find:

$$A_i - A = 4\pi g_i k^{-1}\rho \quad \ldots\ldots\ldots\ldots\ldots\ldots (14.6)$$

SECTION 15

The Thermo-Electric Effect in Crystals

It should be possible for an electric field to be set up by a temperature gradient. Let us assume that the vector T is the temperature gradient and is related to the vector field E through the matrix Π by means of the equation:

$$E = \Pi T \quad \text{where} \quad \Pi = \begin{pmatrix} \Pi_{11} & \Pi_{12} & \Pi_{13} \\ \Pi_{21} & \Pi_{22} & \Pi_{23} \\ \Pi_{31} & \Pi_{32} & \Pi_{33} \end{pmatrix} \quad \ldots\ldots\ldots (15.1)$$

Examination shows that Π transforms through

$$\Pi' = a\Pi a_c \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (15.2)$$

For Class 1 the Π matrix has the 9 terms of (15.1). Class 2 has a center of symmetry. For a center of symmetry $a = -I$ but $a = -I$ causes no change in (15.2) so that class 2 has 9 constants. The thermo electro effect is not killed by the presence of a center of symmetry. The ordinary thermo-electric effect of metals is a case in point.

If x_3 is a binary axis $a = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$ and Π reduces to

$$\Pi = \begin{pmatrix} \Pi_{11} & \Pi_{12} & 0 \\ \Pi_{21} & \Pi_{22} & 0 \\ 0 & 0 & \Pi_{33} \end{pmatrix} \quad \ldots\ldots\ldots\ldots\ldots\ldots (15.3)$$

Examination shows this form to answer for classes 3 and 4 and 5.

If x_1 and x_3 are binary (15.3) reduces to

$$\Pi = \begin{pmatrix} \Pi_{11} & 0 & 0 \\ 0 & \Pi_{22} & 0 \\ 0 & 0 & \Pi_{33} \end{pmatrix} \quad \ldots\ldots\ldots\ldots\ldots\ldots (15.4)$$

which described classes 6, 7 and 8.

For x_3 quarternary alternating:

$$\Pi = \begin{pmatrix} \Pi_{11} & \Pi_{12} & 0 \\ -\Pi_{12} & \Pi_{11} & 0 \\ 0 & 0 & \Pi_{33} \end{pmatrix} \quad \ldots\ldots\ldots\ldots\ldots\ldots (15.5)$$

This is found to handle classes 9 and 10. If x_3 is quarternary alternating and x_1 is binary:

$$\Pi = \begin{pmatrix} \Pi_{11} & 0 & 0 \\ 0 & \Pi_{11} & 0 \\ 0 & 0 & \Pi_{33} \end{pmatrix} \quad \ldots\ldots\ldots\ldots\ldots\ldots (15.6)$$

which is found to cover classes 11, 12, 13, 14 and 15. For classes 16, 17, 19, 23 and 25 Π reduces to the form (15.5).

If x_3 is trigonal and x_1 is binary the matrix is (15.5) which then handles cases 18, 20, 21, 22, 24, 26 and 27.

For cubic crystals, not only are x_1x_2 and x_3 binary as for matrix (15.4) but the vector $\begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}$ is an A_3, for which $a = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}$ whence, for classes 28, 29, 30 and 31 we find the matrix:

$$\Pi = \begin{pmatrix} \Pi_{11} & 0 & 0 \\ 0 & \Pi_{11} & 0 \\ 0 & 0 & \Pi_{11} \end{pmatrix} \quad \ldots\ldots\ldots\ldots\ldots\ldots (15.6)$$

Reports of a pyro electric effect in quartz should probably be attributed to nonuniform heating exciting the piezo electric effect. Reports of a pyro electric effect in such crystals as topaz and colemanite which have a center of symmetry and hence cannot be piezo electric should probably be attributed to this thermo electric effect.

SECTION 16

The Propagation of Light in Crystalline Media

Maxwell's equations are:

$$C\nabla \times B = 4\pi j$$

$$C\nabla \times E = -B$$

when C is the velocity of light in free space, E is the (vector) electric field, j is the induction current and B is the magnetic induction. In a crystalline medium the current is given by $4\pi j = k\dot{E}$ where k is the dielectric constant (matrix), whence:

$$C\nabla \times B = k\dot{E} \quad \ldots\ldots (16.1)$$

$$C\nabla \times E = -\dot{B} \quad \ldots\ldots (16.2)$$

As the divergence of the Curl is always zero:

$$\begin{aligned} \nabla_c k\dot{E} &= \nabla_c j = 0 \\ \nabla_c B &= 0 \end{aligned} \quad \ldots\ldots (16.3)$$

applying $\frac{\partial}{\partial t}$ to (16.1) and substituting (16.2) in the result:

$$-C^2\nabla \times \nabla \times E = k\ddot{E} \quad \text{or}$$

$$C^2(\nabla_c\nabla - \nabla\nabla_c)E = k\ddot{E} \quad \ldots\ldots (16.4)$$

We shall try as a solution:

$$\dot{E} = \dot{E}_0 e^{i(qn_c r - \omega t)} \quad \ldots\ldots (16.5)$$

where E_0 is the vector amplitude of the electric field, i is $\sqrt{-1}$, r is the radius vector from the origin to any point, q is a constant, n is the unit normal (at r) of surfaces of equal phase, and ω is 2π times the frequency of E.

Substituting (16.5) in (16.4) we find:

$$\dot{E} - n\dot{E}_c n = \frac{\omega^2}{q^2 c^2} k\dot{E} \quad \ldots\ldots (16.6)$$

Examination of (16.5) shows that $\frac{\omega}{q}$ is the phase velocity along n. Writing $4\pi k^{-1} j$ for $\dot{E}$ and V^2 for $\frac{\omega^2}{q^2}$ we have:

$$k^{-1}j - nj_c k^{-1} n = \frac{V^2}{c^2} j \quad \ldots\ldots (16.7)$$

This equation is independent of the absolute value of j so let us restrict j to being a unit vector.

$$\nabla_c k\dot{E} = 0 = \nabla_c k\dot{E}_0 e^{i(qn_c r - \omega t)} = j_c niq e^{i(qn_c r - \omega t)}$$

whence $$j_c n = 0 \quad \ldots\ldots (16.8)$$

That is, the current is always normal to the direction of propagation.

Multiplying (16.7) thru by the prefactor j_c and cancelling the term in $j_c n$ we have:

$$j_c k^{-1} j = \frac{V^2}{c^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots (16.9)$$

This tells us that the velocity is a single valued function of the direction of the current.

With the idemfactor I, (16.7) may be written:

$$\left(k^{-1} - \frac{V^2}{c^2} I\right) j = n(k^{-1} j)_c n$$

If we multiply this thru by $\left(k^{-1} - \frac{V^2}{c^2} I\right)^{-1}$ we get

$$j = \left(k^{-1} - \frac{V^2}{c^2} I\right)^{-1} n(k^{-1} j)_c n \quad \ldots\ldots\ldots\ldots (16.10)$$

Multiplying this thru by n_c and dropping the scalar factor $(k^{-1} j)_c n$:

$$n_c \left(k^{-1} - \frac{V^2}{c^2} I\right)^{-1} n = 0 \quad \ldots\ldots\ldots\ldots (16.11)$$

If the axes are so chosen that k is a diagonal matrix (16.9) and (16.11) become:

$$\frac{V^2}{c^2} = \frac{j_1^2}{k_{11}} + \frac{j_2^2}{k_{22}} + \frac{j_3^2}{k_{33}} \quad \ldots\ldots\ldots\ldots\ldots (16.12)$$

$$\frac{n_1^2}{\frac{1}{k_{11}} - \frac{V^2}{C^2}} + \frac{n_2^2}{\frac{1}{k_{22}} - \frac{V^2}{C^2}} + \frac{n_3^3}{\frac{1}{k_{33}} - \frac{V^2}{C^2}} = 0 \quad \ldots\ldots\ldots (16.13)$$

Examination of (16.13) shows that (16.11) must have two values of V^2 for each value of the vector normal n. As V^2 is a single valued function of j there must be two distinct values of j (j' and j'' say) for any particular n; and given n, only waves having their current vectors in the directions of j' and j'' can be propagated. A ray in the direction N but not having its j in one of the directions j' or j'' will be broken up into two components having their current vectors along j' and j'' respectively.

If the velocity V_1 corresponds to j' and V_2 to j'' we have by means of (16.10) since $n' = n''$:

$$j_c' j'' = n_c \left(k^{-1} - \frac{V_1^2}{c^2} I\right)_c^{-1} \left(k^{-1} - \frac{V_2^2}{c^2} I\right)^{-1} n(k^{-1} j')_c n(k^{-1} j'')_c n$$

(The quantities in the braces are scalar)

By means of the identity

$$(u^{-1} - v^{-1}) = -u^{-1}(u - v)v^{-1}$$

since

$$k^{-1} - \frac{V_1^2}{c^2} I - \left(k^{-1} - \frac{V_2^2}{c^2} I\right) = \frac{V_2^2 - V_1^2}{c^2} I$$

the idemfactor can be multiplied into an adjacent matrix giving

$$n_c \left(k^{-1} - \frac{V_1^2}{c^2} I\right)^{-1} \left(k^{-1} - \frac{V_2^2}{c^2} I\right)^{-1} n$$

$$= \frac{c^2}{V_2^2 - V_1^2} n_c \left(k^{-1} - \frac{V_1^2}{c^2} I\right)^{-1} - \left(k^{-1} - \frac{V_2^2}{c^2} I\right)^{-1} n$$

$$= 0 - 0 = 0$$

so that j' and j'' are mutually perpendicular.

SECTION 17

The Electro-Optic Effect

The velocity of light in a crystalline medium is a single valued function of the unit current vector j

$$\frac{V^2}{c^2} = j_c k^{-1} j \quad \ldots\ldots\ldots\ldots\ldots\ldots (16.11)$$

where c is the velocity of light in vacuo and k is the dielectric matrix, also $j = \dot{D}$ where $\dot{D}$ is $\frac{dD}{dt}$.

We developed the induction as a linear function of the electric field, deriving the relation:

$$4\pi D = kE \quad \ldots\ldots\ldots\ldots\ldots\ldots (6.1)$$

If the induction is not a linear function of the electric field we can improve on eq. (6.1) by adding second order terms:

$$4\pi D_i = k_{i1}E_1 + k_{i2}E_2 + k_{i3}E_3 + k_{i1}E_1^2 + k_{i2}E_2^2 + k_{i3}E_3^2 + \tfrac{1}{2} h_{i4}E_2E_3 + \tfrac{1}{2} h_{i4}E_3E_2 + \ldots \tfrac{1}{2} h_{i6}E_1E_2$$

or

$$4\pi D_i = (k_{i1} + h_{i1}E_1 + \tfrac{1}{2} h_{i6}E_2 + \tfrac{1}{2} h_{i5}E_3)\, E_1 + (k_{i2} + \tfrac{1}{2} h_{i6}E_1 + h_{i2}E_2 + \tfrac{1}{2} h_{i4}E_3)\, E_2 + (k_{i3} + \tfrac{1}{2} h_{i5}E_1 + \tfrac{1}{2} h_{i4}E_2 + h_{i3}E_3)\, E_3 \quad \ldots\ldots\ldots\ldots (17.1)$$

Examination of (17.1) suggests that we might consider the k's as being lineraly modified by the field. Writing k as a single column matrix:

$$K = \begin{pmatrix} k_{11} \\ k_{22} \\ k_{33} \\ \\ k_{23} \\ k_{13} \\ k_{12} \end{pmatrix} = \begin{pmatrix} K_1 \\ K_2 \\ \cdot \\ \\ \cdot \\ \cdot \\ K_6 \end{pmatrix}$$

we may write

$$K = K^\circ + h\,E \qquad (17.2)$$

where K° is the dielectric matrix for vanishingly small fields.

We can develop the modified reciprocal matrix in the same manner:

$$k^{-1} = \begin{pmatrix} k_{11}^{-1} & k_{12}^{-1} & k_{13}^{-1} \\ k_{12}^{-1} & k_{22}^{-1} & k_{23}^{-1} \\ k_{13}^{-1} & k_{23}^{-1} & k_{33}^{-1} \end{pmatrix} \qquad K^{-1} = \begin{pmatrix} K_1^{-1} \\ K_2^{-1} \\ \cdot \\ \cdot \\ \cdot \\ K_6^{-1} \end{pmatrix} = \begin{pmatrix} k_{11}^{-1} \\ k_{22}^{-1} \\ k_{33}^{-1} \\ k_{22}^{-1} \\ k_{13}^{-1} \\ k_{12}^{-1} \end{pmatrix}$$

where

$$K^{-1} = K^{-1^\circ} + zE \qquad (17.3)$$

It is to be noted that K^{-1} is not the reciprocal of K but merely a symbol for the single column matrix formed from k^{-1} in the usual way. Taking reciprocals of both sides of $k' = \alpha k a_c$ we find $(k^{-1})' = \alpha k^{-1} a_c$. That is, k^{-1} transforms exactly as did k. Whence, K^{-1} transforms exactly as K does, i. e.

$$K^{-1'} = \alpha\, K^{-1}$$

We can rewrite (17.3) as

$$\alpha\, K^{-1} = \alpha\, K^{-1^\circ} + (\alpha\, z a_c)\, aE$$

or

$$K^{-1'} = (K^{-1^\circ})' + z'E'$$

$$z' = \alpha\, z a_c \qquad (17.4)$$

In case $\alpha^{-1} = \alpha c$ the z's transform as do the conjugates of the piezoelectric constants, d. Of the transformations permitted by the symmetry

of the 32 crystal classes only those of the trigonal and hexagonal systems fail to have $\alpha^{-1} = \alpha_c$. These 12 classes must be examined individually but the other classes may have their z matrices copied from the corresponding d_c matrices.

Applying $z' = \alpha z a_c$ for a rotation of 120° about x_3 we find for class 16

$$z = \begin{pmatrix} z_{11} & -z_{22} & z_{13} \\ -z_{11} & z_{22} & z_{13} \\ 0 & 0 & z_{33} \\ z_{41} & z_{51} & 0 \\ z_{51} & -z_{41} & 0 \\ -z_{22} & -z_{11} & 0 \end{pmatrix}$$

The remaining 11 classes may be derived from class 16 by operations for which either $\alpha^{-1} = \alpha_c$ or a center of symmetry exists. Consequently, we may form our z matrices from the d_c's in all cased *if we leave out the* 2's.

The electro-optic effect can be put in terms of the polarization instead of the field by substituting in (17.3).

$$E = 4\pi\,(k-I)^{-1}\,P \quad \text{whence}$$

$$K^{-1} = K^{-1^\circ} + \eta P \qquad (17.5)$$

where

$$\eta = 4\pi z(k - I)^{-1}$$

Conversely

$$z = \frac{1}{4\pi}\,\eta\,(k - I) \qquad (17.6)$$

The η matrices transform exactly as did the z's and hence may be formed from the d_c's but omitting the 2's.

SECTION 18

The Piezo-Optical Effect

If the dielectric constants of a crystal are changed by the application of stress, this may be represented by:

$$K^{-1} = (K^{-1})^\circ + \pi X \qquad (18.1)$$

where the 36 constants $\pi_{11} \cdots \pi_{66}$ are stress-optical constants.

We may then form k^{-1} as

$$k^{-1} = \begin{pmatrix} k_{11}^{-1} + \pi_{1i}X_i, & k_{12}^{-1} + \pi_{6i}X_i, & k^{-1} + \pi_{5i}X_i \\ k_{12}^{-1} + \pi_{6i}X_i, & k_{22}^{-1} + \pi_{2i}X_i, & k_{23}^{-1} + \pi_{4i}X_i \\ k_{13}^{-1} + \pi_{5i}X_i, & k_{23}^{-1} + \pi_{4i}X_i, & k_{33}^{-1} + \pi_{3i}X_i \end{pmatrix} \qquad (18.2)$$

As the velocity of a light ray of unit current vector j is given by

$$j_c k^{-1} j = \frac{V^2}{c^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots (16.9)$$

We can, by (18.2) and (16.9), compute the change in the velocity caused by the stress, if we know the constants π.

Altering (18.1) to $\alpha K^{-1} = \alpha K^{-1^\circ} + \alpha\pi\alpha^{-1}\alpha X$ we see that:

$$K^{-1'} = K^{-1^\circ} + \pi' X' \quad \text{where} \quad \pi' = \alpha\pi\alpha^{-1} \quad \ldots\ldots\ldots (18.3)$$

The alteration of K^{-1} can be expressed as a function of the strain by substituting ce for X in (18.1).

$$K^{-1} = K^{-1^\circ} + \pi ce = K^{-1^\circ} + me \quad \ldots\ldots\ldots\ldots (18.4)$$

$$m = \pi c, \qquad \pi = ms \quad \ldots\ldots\ldots\ldots\ldots\ldots (18.5)$$

Operating in (18.4) as we did on (18.1) we find m transforms as

$$m' = \alpha m \alpha_c \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (18.6)$$

Applying the crystal symmetry operation to these matrices shows that they reduce to the following

Triclinic system
36 constants

$$\begin{pmatrix} \pi_{11} & \pi_{12} & \pi_{13} & \pi_{14} & \pi_{15} & \pi_{16} \\ \pi_{21} & \pi_{22} & \pi_{23} & \pi_{24} & \pi_{25} & \pi_{26} \\ \pi_{31} & \pi_{32} & \pi_{33} & \pi_{34} & \pi_{35} & \pi_{36} \\ \pi_{41} & \pi_{42} & \pi_{43} & \pi_{44} & \pi_{45} & \pi_{46} \\ \pi_{51} & \pi_{52} & \pi_{53} & \pi_{54} & \pi_{55} & \pi_{56} \\ \pi_{61} & \pi_{62} & \pi_{63} & \pi_{64} & \pi_{65} & \pi_{66} \end{pmatrix}$$

The m matrix is entirely analogous

$\ldots\ldots\ldots\ldots\ldots (18.7)$

Monoclinic system
x_3 is binary
20 constants

$$\begin{pmatrix} \pi_{11} & \pi_{12} & \pi_{13} & 0 & 0 & \pi_{16} \\ \pi_{21} & \pi_{22} & \pi_{23} & 0 & 0 & \pi_{26} \\ \pi_{31} & \pi_{32} & \pi_{33} & 0 & 0 & \pi_{36} \\ 0 & 0 & 0 & \pi_{44} & \pi_{45} & 0 \\ 0 & 0 & 0 & \pi_{54} & \pi_{55} & 0 \\ \pi_{61} & \pi_{62} & \pi_{63} & 0 & 0 & \pi_{66} \end{pmatrix}$$

The m matrix is entirely analogous

$\ldots\ldots\ldots\ldots\ldots (18.8)$

Orthorhombic system x_3 is binary
12 constants

$$\begin{pmatrix} \pi_{11} & \pi_{12} & \pi_{13} & 0 & 0 & 0 \\ \pi_{21} & \pi_{22} & \pi_{23} & 0 & 0 & 0 \\ \pi_{31} & \pi_{32} & \pi_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & \pi_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & \pi_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & \pi_{66} \end{pmatrix}$$

The m matrix is entirely analogous (Rochelle salt)

$\ldots\ldots\ldots\ldots\ldots (18.9)$

Tetragonal system
x_3 is a four-fold axis
(Classes 9, 10 & 13)
9 Constants

$$\begin{pmatrix} \pi_{11} & \pi_{12} & \pi_{13} & 0 & 0 & \pi_{16} \\ \pi_{12} & \pi_{11} & \pi_{13} & 0 & 0 & -\pi_{16} \\ \pi_{31} & \pi_{31} & \pi_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & \pi_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & \pi_{44} & 0 \\ \pi_{61} & -\pi_{61} & 0 & 0 & 0 & \pi_{66} \end{pmatrix}$$

The m matrix is entirely analogous

.....(18.10)

Tetragonal system
x_3 is a four-fold axis
x_1 is a binary axis
(Classes 11, 12, 14 & 15)
7 Constants

$$\begin{pmatrix} \pi_{11} & \pi_{12} & \pi_{13} & 0 & 0 & 0 \\ \pi_{12} & \pi_{11} & \pi_{13} & 0 & 0 & 0 \\ \pi_{31} & \pi_{31} & \pi_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & \pi_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & \pi_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & \pi_{66} \end{pmatrix}$$

The m matrix is entirely analogous

.....(18.11)

Trigonal system
x_3 is a trigonal axis
(Classes 16 & 17)
11 Constants

$$\begin{pmatrix} \pi_{11} & \pi_{12} & \pi_{13} & \pi_{14} & -\pi_{25} & 0 \\ \pi_{12} & \pi_{11} & \pi_{13} & -\pi_{14} & \pi_{25} & 0 \\ \pi_{31} & \pi_{31} & \pi_{33} & 0 & 0 & 0 \\ \pi_{41} & \pi_{41} & 0 & \pi_{44} & \pi_{45} & 2\pi_{52} \\ -\pi_{52} & \pi_{52} & 0 & -\pi_{45} & \pi_{44} & 2\pi_{41} \\ 0 & 0 & 0 & \pi_{25} & \pi_{14} & (\pi_{11} - \pi_{12}) \end{pmatrix}$$

The m matrix is analogous except that

$$m_{46} = m_{52}$$
$$m_{56} = m_{41}$$
$$m_{66} = \frac{m_{11} - m_{12}}{2}$$

.....(18.12)

Trigonal system
x_3 is a trigonal axis
x_1 is a binary axis
(Classes 18, 20 & 21)
8 Constants

$$\begin{pmatrix} \pi_{11} & \pi_{12} & \pi_{13} & \pi_{14} & 0 & 0 \\ \pi_{12} & \pi_{11} & \pi_{13} & -\pi_{14} & 0 & 0 \\ \pi_{31} & \pi_{31} & \pi_{33} & 0 & 0 & 0 \\ \pi_{41} & -\pi_{41} & 0 & \pi_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & \pi_{44} & 2\pi_{41} \\ 0 & 0 & 0 & 0 & \pi_{14} & (\pi_{11} - \pi_{12}) \end{pmatrix}$$

The m matrix is analogous except that

$$m_{56} = m_{41}$$
$$m_{66} = \frac{m_{11} - m_{12}}{2}$$

(quartz)

.....(18.13)

Hexagonal system
x_3 is a sixfold axis
x_1 is a binary axis
(Classes 19, 22, 23, 24, 25, 26 & 27)
6 Constants

$$\begin{pmatrix} \pi_{11} & \pi_{12} & \pi_{13} & 0 & 0 & 0 \\ \pi_{12} & \pi_{11} & \pi_{13} & 0 & 0 & 0 \\ \pi_{31} & \pi_{31} & \pi_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & \pi_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & \pi_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & (\pi_{11} - \pi_{12}) \end{pmatrix}$$

The m matrix is analogous except that

$$m_{66} = \frac{m_{11} - m_{12}}{2}$$

.....(18.14)

Cubic system
3 Constants

$$\begin{pmatrix} \pi_{11} & \pi_{12} & \pi_{12} & 0 & 0 & 0 \\ \pi_{12} & \pi_{11} & \pi_{12} & 0 & 0 & 0 \\ \pi_{12} & \pi_{12} & \pi_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & \pi_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & \pi_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & \pi_{44} \end{pmatrix}$$

The m matrix is entirely analogous

.....(18.15)

For isotropic bodices, the π matrix is formed by setting $\pi_{44} = (\pi_{11} - \pi_{12})$ in the π matrix of the cubic system; the m matrix is similarly formed by putting $m_{44} = \dfrac{m_{11} - m_{12}}{2}$.

Isotropic bodies

$$\begin{pmatrix} \pi_{11} & \pi_{12} & \pi_{12} & 0 & 0 & 0 \\ \pi_{12} & \pi_{11} & \pi_{12} & 0 & 0 & 0 \\ \pi_{12} & \pi_{12} & \pi_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & \pi_{11}-\pi_{12} & 0 & 0 \\ 0 & 0 & 0 & 0 & \pi_{11}-\pi_{12} & 0 \\ 0 & 0 & 0 & 0 & 0 & \pi_{11}-\pi_{12} \end{pmatrix}$$

The m matrix has m_{44} etc $= \dfrac{m_{11}-m_{12}}{2}$ .....(18.16)

SECTION 19

Application of the Electro and Piezo Optical Effect

In the equations $K^{-1} = K^{-1^\circ} + zE$ and $K^{-1} = K^{-1^\circ} + mE$, etc. the K^{-1}'s are to be used in forming k^{-1} for the equation giving the velocity of the light used namely $\dfrac{V^2}{C^2} = j_c k^{-1} j$. Obviously then K^{-1° should be formed from the squares of the reciprocals of the refractive indices, the lower three members being zero. After applying the electric field or strain a transformation of coordinates may be necessary to rediagonalize, i.e. make $K_4^{-1'} = K_5^{-1'} = K_6^{-1'} = 0$. From the rediagonalized K^{-1} we may write the new principle refractive indices by taking the reciprocals of the square roots of $K_1^{-1'}$, $K_2^{-1'}$ and $K_3^{-1'}$. It should be noted that if $K_i^{-1'} = K_i^{-1^\circ} + \Delta_i$ then

$$\mu_i' + \Delta\mu_i = \mu_i' - \frac{\mu_i'^3}{2}\Delta_i \quad \text{.....(19.1)}$$

For a given direction of the wave normal there are two velocities, a wave splitting into two components traveling with different velocities. By definition the refractive indices, μ_a and μ_b in a given direction are the normal velocities in that direction divided into the velocity of light in free space. Whence in a path length l there are $\dfrac{l\mu_a}{\lambda}$ waves in one component and $\dfrac{l\mu_b}{\lambda}$ waves in the other, where λ is the wave-length in vacuum. Consequently if l is the thickness of the crystal along that path the two components can recombine after passing through the medium but they are out of phase by $\gamma = \dfrac{l}{\lambda}(\mu_a - \mu_b)$ whole waves so that the light which entered as plane polarized will leave elliptically or circularly polarized, except when 2γ is an integer.

The quantity $B = \mu_a - \mu_b$ is known as the birefringence.

$$\gamma = \frac{lB}{\lambda} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (19.2)$$

If a phase difference of $\frac{1}{30}$ wave can be just detected, using a wave length of 6000 $\mathring{A}$ and a path length $l = 1$ cm the just detectable birefringence would be $B = \frac{\gamma\lambda}{l} = 2 \times 10^{-6}$; if the path were 10 cms the detectable B would be 0.2×10^{-6}. Obviously this detectable difference between refractive indices is much smaller than could be detected by measuring each refractive index and subtracting.

It is customary to choose the coordinate system so that looking along x_2 the very lowest refractive index is for polarization in the plane of x_1 and the very highest for polarization in the plane of x_3. That is, the x_2 axis is the axis along which light should be passed to get the greatest birefringence.

Birefringence in any Direction

If the axes are so chosen that K is diagonal and $K_3 > K_2 > K_1$ then, somewhere in the plane perpendicular to x_2 are two directions, the optic axes, along which there is a single normal velocity. These directions make* equal angles V with the x_3 axis where

$$\sin V = \pm\sqrt{\frac{K_1^{-1} - K_2^{-1}}{K_1^{-1} - K_3^{-1}}}$$

or

$$\cos V = \pm\sqrt{\frac{K_2^{-1} - K_3^{-1}}{K_1^{-1} - K_3^{-1}}} \quad \ldots\ldots\ldots\ldots\ldots (19.3)$$

Also the two refractive indices μ_a and μ_b for a wave normal making angles g_1 and g_2 with these optic axes satisfy the equation:

$$\frac{2}{\mu_a^2} = (K_1^{-1} + K_3^{-1}) + (K_1^{-1} - K_3^{-1}) \cos (g_1 - g_2)$$

$$\frac{2}{\mu_b^2} = (K_1^{-1} + K_3^{-1}) + (K_1^{-1} - K_3^{-1}) \cos (g_1 + g_2)$$

whence

$$2\left(\frac{1}{\mu_a^2} - \frac{1}{\mu_b^2}\right) = \frac{2(\mu_b - \mu_a)(\mu_a + \mu_b)}{\mu_a^2 \mu_b^2}$$

$$= (K_1^{-1} - K_3^{-1}) \cos (g_1 - g_2) - \cos (g_1 + g_2)$$

* Theory of Optics, P. Drude, pg. 320.

as $B = \mu_b - \mu_a$ is the birefringence we have:

$$B = \frac{\mu_a^2 \mu_b^2}{\mu_a + \mu_b} (K_1^{-1} - K_3^{-1}) \sin g_1 \sin g_2 \quad \ldots\ldots\ldots (19.4)$$

By spherical trigonometry:

$$\begin{aligned} \cos g_1 &= \cos V \cos\theta + \sin V \sin\theta \cos\phi \\ \cos g_2 &= \cos V \cos\theta - \sin V \sin\theta \cos\phi \end{aligned} \quad \ldots\ldots\ldots (19.5)$$

where θ is the angle the wave normal makes with x_3 and ϕ is the angle the plane containing the normal and x_3 makes with x_1.

From (19.5) it follows that:

$\sin g_1 \sin g_2 =$

$$\sqrt{(1 - \cos^2 V \cos^2\theta - \sin^2 V \sin^2\theta \cos^2\phi)^2 - 4 \sin^2 V \cos^2 V \sin^2\theta \cos^2\theta \cos^2\phi} \quad \ldots\ldots (19.6)$$

Hence if the rediagonalized K^{-1} is

$$\begin{pmatrix} K_1^{-1^\circ} + \Delta_1 \\ K_2^{-1^\circ} + \Delta_2 \\ K_3^{-1^\circ} + \Delta_3 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

then

$$B = \frac{\mu_a^2 \mu_b^2}{\mu_a - \mu_b}$$

$$\sqrt{\begin{aligned} &(K_1^{-1^\circ} - K_3^{-1^\circ} + \Delta_1 - \Delta_3) - (K_2^{-1^\circ} - K_3^{-1^\circ} + \Delta_2 - \Delta_3) \cos^2\theta \\ &- (K_1^{-1^\circ} - K_2^{-1^\circ} + \Delta_1 - \Delta_2) \sin^2\theta \cos^2\phi^2 - 4(K_1^{-1^\circ} - K_2^{-1^\circ} \\ &+ \Delta_1 - \Delta_2)(K_3^{-1^\circ} - K_3^{-1^\circ} + \Delta_2 - \Delta_3) \sin^2\theta \cos^2\theta \cos^2\phi \end{aligned}} \quad \ldots (19.7)$$

$$B = B_0 + \frac{\mu^3}{2} (\Delta_1 \Delta_3) \sin g_1 \sin g_2 \quad \ldots\ldots\ldots\ldots (3')$$

For most practical purposes we may take

$$\frac{\mu_a^2 \mu_b^2}{\mu_a + \mu_b} = \frac{\mu^3}{2}$$

where μ is some intermediate value of the refractive index.*

* *Note*: It might seem that as $K_i^{-1} = K_i^{-1^0} + \Delta_i$ gives us $\mu_i = \mu_i^0 - \frac{\mu_i^2}{2}\Delta_i + \frac{3}{8}\mu_i^5 \Delta_i^2 \cdots$ we could form the 3 principal birefringences directly from the μ's instead of using $(6a \cdots e)$. From the μ expressions we would get $B_3 = \mu_2 - \mu_1 - \frac{1}{2}(\mu_2^3 \Delta_2 - \mu_1^3 \Delta_1) + \frac{3}{8}$ which differs from $6b$ if $\mu_2 \neq \mu_1$. Equation $6b$ is correct; the one from the μ expression is an approximation.

In a few special cases (18.7) may be simplified. If (ϕ, θ) falls along an optic axis $g_1 = V - V^\circ$ and $g_2 = V + V^\circ$ whence

$$B_A = \frac{\mu^3}{2}[(\Delta_1 - \Delta_2)\cos^2 V^\circ - (\Delta_2 - \Delta_3)\sin^2 V^\circ] \quad (19.61)$$

if $\theta = 0$

$$B = \mu_2 - \mu_1 + \frac{\mu_1^2 \mu_2^2}{\mu_1 + \mu_2}(\Delta_1 - \Delta_2) \quad (19.62)$$

if $\theta = 90^\circ$

$$B = (\mu_3 - \mu_1)(1 - \cos^2\phi \sin^2 V^\circ) + \frac{\mu^3}{2}(\Delta_1 - \Delta_3 - (\Delta_1 - \Delta_2)\cos^2\phi) \quad (19.63)$$

if $\phi = 0$

$$B = (\mu_3 - \mu_1)(\sin^2 V^\circ - \sin^2\theta) + \frac{\mu^3}{2}(\Delta_1 - \Delta_2 - (\Delta_1 - \Delta_3)\sin\theta) \quad (19.64)$$

if $\phi = 90^\circ$

$$B = (\mu_3 - \mu_1)(1 - \cos^2\theta \cos^2 V^\circ) + \frac{\mu^3}{2}(\Delta_1 - \Delta_3 - (\Delta_2 - \Delta_3)\cos\theta) \quad (19.65)$$

The Electro Optics of Quartz

For quartz, in the equation $K^{-1} = K^{-1^\circ} + zE$

$$Z = \begin{pmatrix} z_{11} & 0 & 0 \\ -z_{11} & 0 & 0 \\ 0 & 0 & 0 \\ z_{41} & 0 & 0 \\ 0 & -z_{41} & 0 \\ 0 & -z_{11} & 0 \end{pmatrix}$$

If E is in practical volts*
$Z_{11} = 0.47 \times 10^{-10}$
$Z_{41} = 0.20 \times 10^{-10}$

Obviously the E_3 component produces no effect so we shall examine the effects due to the components E_1 and E_2 separately. If $E = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} E_1$

$$K^{-1} = \begin{pmatrix} K_1^{-1^\circ} + z_{11}E_1 \\ K_1^{-1^\circ} - z_{11}E_1 \\ K_3^{-1^\circ} \\ z_{41}E_1 \\ 0 \\ 0 \end{pmatrix}$$

which can be diagonalized

* Computed from F. Pockels data, see his Lehrbuch der Kristall-Optik, (B. G. Tuebner).

by a small rotation about x_1 of amount $\theta = \dfrac{-z_{41}E_1}{K_1^{-1} - K_3^{-1}}$ giving

$$K^{-1} = \begin{pmatrix} K_1^{-1^\circ} + z_{11}E_1 \\ K_1^{-1^\circ} - z_{11}E_1 \\ K_3^{-1^\circ} \\ 0 \\ 0 \\ 0 \end{pmatrix} \quad \text{and} \quad \mu = \begin{matrix} \mu_1 - \dfrac{\mu_1^3}{2} \times 0.47 \times 10^{-10} E_1 \\ \mu_1 + \dfrac{\mu_1^3}{2} \times 0.47 \times 10^{-10} E_1 \\ \mu_3 \end{matrix}$$

The greatest "added birefringence" is gotten by viewing along x_3, when $\Delta B = 1.544^3 \times 0.47 \times 10^{-10} E_1$. If $E_1 = 10^4$ $\Delta B = 1.73 \times 10^{-6}$ a quantity detectable if the path length is about 1 cm. Viewing along x_3 (the optic axis) is complicated by the rotation of the plane of polarization in quartz. Homogeneous strains have never been found to alter this rotation, but the rotation complicates and partly masks the birefringence phenomena. If $E = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} E_2$ we find

$$K^{-1} = \begin{pmatrix} K_1^{-1^\circ} \\ K_1^{-1^\circ} \\ K_3^{-1^\circ} \\ 0 \\ -z_{41}E_2 \\ -z_{11}E_2 \end{pmatrix}$$

Rotating the coordinate axes through 45° about x_3 then applying the transformation

$$a = \begin{pmatrix} 1 & 0 & \underline{a} \\ 0 & 1 & -\underline{a} \\ -\underline{a} & \underline{a} & 1 \end{pmatrix}$$

where

$$\underline{a} = \frac{-\dfrac{1}{\sqrt{2}} z_{41}E_2}{K_1^{-1} - K_3^{-1}}$$

we find:

$$K^{-1''} = \begin{pmatrix} K_1^{-1^\circ} + z_{11}E_2 \\ K_1^{-1^\circ} - z_{11}E_2 \\ K_3^{-10} \\ 0 \\ 0 \\ 0 \end{pmatrix} \qquad \mu = \begin{matrix} \mu_1 - \dfrac{\mu_1^3}{2} z_{11}E_2 \\ \mu_1 + \dfrac{\mu_1^3}{2} z_{11}E_2 \\ \mu_3 \end{matrix}$$

which is identical to the μ for field along x_1, but the final axes in this case do not coincide with the final axes for $E = E_1$, but again, the greatest added birefringence is utilized by viewing along x_3. In the second case the Nicols would be best set along x_1 and x_2, i.e., at 45° to x_1' and x_2' whereas in the first case they would be best set at 45° to x_1 and x_2.

The strain Optics of Quartz

$$K^{-1} = K^{-1^\circ} + m\epsilon,$$

$$m = \begin{pmatrix} m_{11} & m_{12} & m_{13} & m_{14} & 0 & 0 \\ m_{12} & m_{11} & m_{13} & -m_{14} & 0 & 0 \\ m_{31} & m_{31} & m_{33} & 0 & 0 & 0 \\ m_{41} & m_{41} & 0 & m_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & m_{44} & m_{41} \\ 0 & 0 & 0 & 0 & m_{14} & \dfrac{m_{11} - m_{12}}{2} \end{pmatrix}$$

where*

$$\begin{aligned} m_{11} &= .138 \\ m_{12} &= .250 \\ m_{13} &= .259 \\ m_{14} &= .029 \\ m_{31} &= .258 \\ m_{33} &= .098 \\ m_{41} &= -.042 \\ m_{44} &= -.0685 \end{aligned}$$

If the strain is a simple tension along x_1,

$$K^{-1} = \begin{pmatrix} K_1^{-1^\circ} + m_{11}\underline{\epsilon_1} \\ K_1^{-1^\circ} + m_{12}\underline{\epsilon_1} \\ K_3^{-1^\circ} + m_{41}\underline{\epsilon_1} \\ m_{41}\epsilon_1 \\ 0 \\ 0 \end{pmatrix}$$

which diagonalizes, through a small transformation to:

$$K^{-1'} = \begin{pmatrix} K_1^{-1^\circ} + m_{11}\epsilon_1 \\ K_1^{-1^\circ} + m_{12}\epsilon_1 \\ K_3^{-1^\circ} + m_{31}\epsilon_1 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

applying 18.63 or 18.64 we find the birefringence along x_1 to be:

$$B_{11} = \mu_3 - \mu_1 + \frac{\mu^3}{2}(m_{12} - m_{31})\,\underline{\epsilon_1} = .0091 - .0148\,\underline{\epsilon_1}$$

Similarly the birefringence along x_2 is $B_{12} = .0091 - .225\,\underline{\epsilon_1}$ and $B_{13} = 0 - .207\,\underline{\epsilon_1}$. With a strain of 10^{-4}, which is about a tenth of the breaking strain, B_{13} would be 20.7×10^{-6}, a quantity detectable in a thickness of one millimeter.

The values of $B_{21} \cdots B_{43}$ corresponding to birefringence along x_6 for a tension along x_2 etc., can be computed in just the same way. But $B_{51} \cdots B_{63}$ require rotations of 45° about x_3 to diagonalize, so the birefringences can be computed by setting $\theta = 45°$ in equations (19.6).

* Lehrbuch der Kristalloptik—F. Pockels.

The following table summarizes these simple strain birefringence effects, the rows indicating the strain and the columns the direction of light passage.

$B_0 - .0148\ \underline{e_1}$	$B_0 - .222\ \underline{e_1}$	$.207\ \underline{e_1}$
$B_0 + .222\ \underline{e_2}$	$B_0 - .0148\ \underline{e_2}$	$.207\ \underline{e_2}$
$B_0 - .298\ \underline{e_3}$	$B_0 - .298\ \underline{e_3}$	0
$B_0 + .0536\ \underline{e_4}$	$B_0 - .0536\ \underline{e_4}$	$-.107\ \underline{e_4}$
$(B_0 + 0$	$B_0 + 0$	$-.107\ \underline{e_5})$
$(B_0 + 0$	$B_0 + 0$	$.208\ \underline{e_6})$

(the parentheses indicate the 45° transformations).

A similar table for the electro-optic effect in quartz is

$B_0 - .87 \times 10^{-10} E_1$	$B_0 + .87 \times 10^{-10} E_1$	$1.74 \times 10^{-10} E_1$
$B_0 + 0$	$B_0 + 0$	$1.74 \times 10^{-10} E_1$
$B_0 + 0$	$B_0 + 0$	0

Since a driving voltage of $E_1 = 100$ volts may, due to the building up of oscillations, cause a periodic strain of $e = 10^{-4}$ in a quartz plate, it would seem from the foregoing that 99.99% of any birefringence change must be due to the mechanical effect.

The 18° Cut Crystal

A crystal, the thickness of which is along the electric axis, x_1, the width making an angle $\theta' \doteq 18°$ with the optic axis, x_3, can be caused to oscillate with a simple motion along its length. (If θ' is not about 18° or 72° the oscillation is not a simple extension along the length, as is shown by the node which then lies diagonally across the crystal.) On a set of axes defined by the edges of the crystal block, x_1' being in the direction of the thickness or x_1, x_3' in the direction of the width and makes an angle θ' with x_3, x_2' is the length and makes an angle θ' with x_2; on these block axes the strain is $\underline{e_2'}$. Rotating the axes about x_1' through an angle θ' we find the strain expressed on the crystal axes to be:

$$e = \alpha^{-1} e' = \begin{pmatrix} 0 \\ \cos^2 \theta' \\ \sin^2 \theta' \\ -\sin\ \theta' \cos \theta' \\ 0 \\ 0 \end{pmatrix} \underline{e_2'}$$

whence

$$K^{-1} = K^{-1^\circ} + me \quad \text{gives us}$$

$$K^{-1} = \begin{pmatrix} K_1^{-1^\circ} + (m_{12}\cos^2\theta' + m_{13}\sin^2\theta' - m_{14}\sin\theta'\cos\theta')\underline{e_2'} \\ K_1^{-1^\circ} + (m_{11}\cos^2\theta' + m_{13}\sin^2\theta' + m_{14}\sin\theta'\cos\theta')\underline{e_2'} \\ K_3^{-1^\circ} + (m_{31}\cos^2\theta' + m_{33}\sin^2\theta')\underline{e_2'} \\ \quad - (m_{41}\cos^2\theta' + m_{44}\sin\theta'\cos\varphi')\underline{e_2'} \\ 0 \\ 0 \end{pmatrix}$$

A small transformation removes the 4th term without altering the others to the first power of small quantities.

To obtain the birefringence along the width x_3', we set $\theta = \theta'$ in equation (18.65):

$$B_{3'} = (\mu_3 - \mu_1)\sin^2\theta' + \frac{\mu^3}{2}\left\{m_{12}\cos^2\theta' - m_{11}\cos^4\theta' + (m_{13} - m_{33})\sin^4\theta' - m_{14}\sin^2\theta'\frac{1+\cos^2\theta'}{2} - m_{31}\sin^2\theta'\cos^2\theta'\right\}\underline{e_2'}$$

which, for $\theta' = 18^\circ$ is $B_3' = .00087 + .20\,\underline{e_2'}$

For the birefringence along the length x_2' we set

$\theta = 90^\circ + \theta'$ in (6*e*) giving:

$$B = (\mu_3 - \mu_1)\cos^2\theta' + \frac{\mu^3}{2}\{m_{12}\cos^2\theta' - m_{31}\cos^4\theta' + (m_{13} - m_{11} - m_{33})\sin^2\theta'\cos^2\theta' - m_{14}\sin\theta'\cos\theta'(1+\sin^2\theta')\}\underline{e_2'}$$

which, for $\theta' = 18^\circ$ is $B_2 = .00824 + .049\,\underline{e_2'}$.

SECTION 20

Transverse Isotropy

A material that has identical properties in all directions normal to a given line is called transversely isotropic. Any line parallel to this line may be considered as an axis of transverse isotropy.

Dielectric Properties, Optical Properties, Thermal Expansion

With respect to these, a transversely isotropic material behaves as does a uniaxial crystal, only two constants being needed to describe each. For example, the displacement current in terms of the electric field and the dielec-

tric constant matrix is $D = \frac{1}{4\pi} kE$ where, if x_3 is the axis of transverse isotropy:

$$D = \begin{pmatrix} D_{11} & 0 & 0 \\ 0 & D_{11} & 0 \\ 0 & 0 & D_{33} \end{pmatrix} \quad \ldots\ldots\ldots\ldots\ldots\ldots (20.1)$$

Elasticity

We must find the forms of S and C, (the elastic modulus and elastic constant matrices) that are not changed by rotations about the axis of transverse isotropy. We can simplify the work by starting with the crystal class that has hexagonal symmetry only. On applying the transformation $S' = \alpha_c S \alpha = S$ for arbitrary rotations about X_3 we find no further simplification follows. Hence the S and C matrices can be copied from those for the Hexagonal Pyramidal Class.

The Piezo-Electric Effect

Again choosing x_3 as the axis of transverse isotropy and starting with hexagonal symmetry about X_3 we find that in order to be invariant to all rotations about X_3 the matrix must simplify to:

$$d = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix} \quad \ldots\ldots\ldots\ldots\ldots\ldots (20.2)$$

A pitch solidified in an electric field would probably exhibit this kind of piezo electric behaviour. It might also be expected to show an electro optic effect governed by a matrix like the conjugate of the above matrix.

SECTION 21

Appendix

Transformations

A counterclockwise rotation of the axes through an angle ϕ about the x_1 axis is represented by the matrices a and α as follows (where c is written for cos ϕ and s for sin ϕ):

$$a = \begin{pmatrix} 1 & 0 & 0 \\ 0 & c & s \\ 0 & -s & c \end{pmatrix}, \quad \alpha = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & c^2 & s^2 & 2sc & 0 & 0 \\ 0 & s^2 & c^2 & -2sc & 0 & 0 \\ 0 & -sc & sc & c^2-s^2 & 0 & 0 \\ 0 & 0 & 0 & 0 & c & -s \\ 0 & 0 & 0 & 0 & s & c \end{pmatrix} \quad \ldots\ldots (21.1)$$

A counterclockwise rotation about x_2 is given by:

$$a = \begin{pmatrix} c & 0 & -s \\ 0 & 1 & 0 \\ s & 0 & c \end{pmatrix}, \quad \alpha = \begin{pmatrix} c^2 & 0 & s^2 & 0 & -2sc & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ s^2 & 0 & c^2 & 0 & 2sc & 0 \\ 0 & 0 & 0 & c & 0 & s \\ sc & 0 & -sc & 0 & c^2-s^2 & 0 \\ 0 & 0 & 0 & -s & 0 & c \end{pmatrix} \quad \ldots\ldots (21.2)$$

A counterclockwise rotation about x_3 is given by:

$$a = \begin{pmatrix} c & s & 0 \\ -s & c & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \alpha = \begin{pmatrix} c^2 & s^2 & 0 & 0 & 0 & 2cs \\ s^2 & c^2 & 0 & 0 & 0 & -2cs \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & c & -s & 0 \\ 0 & 0 & 0 & -s & c & 0 \\ -cs & cs & 0 & 0 & 0 & c^2-s^2 \end{pmatrix} \quad \ldots\ldots (21.3)$$

In case one wants only the value of a tensor property in a given direction not all the elements of a and α need be used, but only a row or column. A special case is that of computing such a property in the direction (θ, ϕ) of polar coordinates. The x_1' axis is chosen in this direction; x_2' and x_3' are not determined. Writing c_1 for $\cos\theta$, c_2 for $\cos\phi$, s_1 for $\sin\theta$ and s_2 for $\sin\phi$ the required matrices are

$$a_c = \begin{pmatrix} c_1 s_2 & \cdots \\ s_1 s_2 & \cdots \\ c_2 & \cdots \end{pmatrix}, \quad \alpha^{-1} = \begin{pmatrix} c_1^2 s_2^2 & \cdots \\ s_1^2 s_2^2 & \cdots \\ c_2^2 & \cdots \\ s_1 s_2 c_2 & \cdots \\ c_1 c_2 s_2 & \cdots \\ c_1 s_1 s_2^2 & \cdots \end{pmatrix} \quad \ldots\ldots\ldots (21.4)$$

From these the (11) term can be computed for any tensor.

A few special transformations needed constantly are: A rotation of 180° about x_3:

$$a = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \alpha = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}, \quad \alpha^{-1} = \alpha_c \quad \ldots (21.5)$$

A rotation of 90° about x_3:

$$a = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \alpha = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 \end{pmatrix}, \quad \alpha^{-1} = \alpha_c \quad (21.6)$$

A reflection in the plane perpendicular to x_3:

$$a = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \quad \alpha = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}, \quad \alpha^{-1} = \alpha_c \quad (21.7)$$

A cyclic interchange where x_2 replaces x_1, etc.:
(The line making equal angles with x_1, x_2, and x_3 is a three-fold axis)

$$a = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} \quad \alpha = \begin{pmatrix} 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{pmatrix}, \quad \alpha^{-1} = \alpha_c \quad (21.8)$$

A cyclic interchange, where $-x_3$ replaces x_1, etc.:
(The line making equal angles with x_1, x_2, and x_3 is a six-fold axis of the second sort)

$$a = \begin{pmatrix} 0 & -1 & 0 \\ 0 & 0 & -1 \\ -1 & 0 & 0 \end{pmatrix}, \quad \alpha = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 \end{pmatrix}, \quad \alpha^{-1} = \alpha_c \quad (21.9)$$

A rotation of 90° about x_3 combined with a reflection in the x_3 plane:

$$a = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \quad \alpha = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 \end{pmatrix}, \quad \alpha^{-1} = \alpha_c \quad (21.10)$$

A rotation of 60° about x_3:

$$\alpha = \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \alpha = \begin{pmatrix} \frac{1}{4} & \frac{3}{4} & 0 & 0 & 0 & \frac{\sqrt{3}}{2} \\ \frac{3}{4} & \frac{1}{4} & 0 & 0 & 0 & \frac{\sqrt{3}}{2} \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ 0 & 0 & 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ -\frac{\sqrt{3}}{4} & \frac{\sqrt{3}}{4} & 0 & 0 & 0 & -\frac{1}{2} \end{pmatrix} \quad \ldots(21.11)$$

To form α^{-1} substitute $-\sqrt{3}$ for $\sqrt{3}$ in α.

A rotation of 60° about x_3 combined with a reflection in x_3:

$$a = \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad \alpha = \begin{pmatrix} \frac{1}{4} & \frac{3}{4} & 0 & 0 & 0 & \frac{\sqrt{3}}{2} \\ \frac{3}{4} & \frac{1}{4} & 0 & 0 & 0 & -\frac{\sqrt{3}}{2} \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ -\frac{\sqrt{3}}{4} & \frac{\sqrt{3}}{4} & 0 & 0 & 0 & -\frac{1}{2} \end{pmatrix} \quad \ldots(21.12)$$

To form α^{-1} substitute $-\sqrt{3}$ for $\sqrt{3}$ in α.

A rotation of 120° about x_3:

$$a = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \alpha = \begin{pmatrix} \frac{1}{4} & \frac{3}{4} & 0 & 0 & 0 & -\frac{\sqrt{3}}{2} \\ \frac{3}{4} & \frac{1}{4} & 0 & 0 & 0 & \frac{\sqrt{3}}{2} \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ 0 & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ \frac{\sqrt{3}}{4} & -\frac{\sqrt{3}}{4} & 0 & 0 & 0 & -\frac{1}{2} \end{pmatrix} \quad \ldots(21.13)$$

To form α^{-1} substitute $-\sqrt{3}$ for $\sqrt{3}$ in α.

Inversion through the origin (a center of symmetry)

$$a = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad \alpha = \begin{pmatrix} 1&0&0&0&0&0 \\ 0&1&0&0&0&0 \\ 0&0&1&0&0&0 \\ 0&0&0&1&0&0 \\ 0&0&0&0&1&0 \\ 0&0&0&0&0&1 \end{pmatrix} = I \quad \alpha^{-1} = \alpha_c \quad \ldots\ldots\ldots (21.14)$$

A rotation of 180° about x_1:

$$a = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad \alpha = \begin{pmatrix} 1&0&0&0&0&0 \\ 0&1&0&0&0&0 \\ 0&0&1&0&0&0 \\ 0&0&0&1&0&0 \\ 0&0&0&0&-1&0 \\ 0&0&0&0&0&-1 \end{pmatrix} \quad \alpha^{-1} = \alpha_c \quad \ldots (21.15)$$

A reflection in x_1 plane:

$$a = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \alpha = \begin{pmatrix} 1&0&0&0&0&0 \\ 0&1&0&0&0&0 \\ 0&0&1&0&0&0 \\ 0&0&0&1&0&0 \\ 0&0&0&0&-1&0 \\ 0&0&0&0&0&-1 \end{pmatrix} \quad \alpha^{-1} = \alpha_c \quad \ldots (21.16)$$

A reflection in the x_2 plane:

$$a = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \alpha = \begin{pmatrix} 1&0&0&0&0&0 \\ 0&1&0&0&0&0 \\ 0&0&1&0&0&0 \\ 0&0&0&-1&0&0 \\ 0&0&0&0&1&0 \\ 0&0&0&0&0&-1 \end{pmatrix} \quad \alpha^{-1} = \alpha = \alpha_c \quad \ldots (21.17)$$

In computing the electro-optic and mechanico-optic effects we need a transformation that will restore to diagonality a matrix that has very small but symmetrical off diagonal terms. This transformation we call a small transformation. Such a transformation has its matrix differing but slightly from an idemfactor.

If $$\bar{k} = \begin{pmatrix} k_{11} + \Delta_{11} & \Delta_{12} & \Delta_{31} \\ \Delta_{12} & k_{22} + \Delta_{22} & \Delta_{23} \\ \Delta_{31} & \Delta_{23} & k_{33} + \Delta_{33} \end{pmatrix}$$

we assume that it can be rediagonalized to the matrix k' by means of the transformation: $k' = \delta\bar{k}\delta_c$ where $\delta = \begin{pmatrix} 1 & \delta_{12} & \delta_{13} \\ \delta_{21} & 1 & \delta_{23} \\ \delta_{31} & \delta_{32} & 1 \end{pmatrix}$

Since $\delta_{11}\,\delta_{21} + \delta_{12}\,\delta_{22} + \delta_{13}\,\delta_{23} = 0$ we find that, to the first order of small quantities $\delta_{ij} = -\delta_{ji}$.

Expanding $\delta\bar{k}\delta_c$ to the first order of small quantities and equating the non-diagonal terms to zero we find that:

$$\delta_{12} = \frac{\Delta_{12}}{k_{11} - k_{22}}; \qquad \delta_{23} = \frac{\Delta_{23}}{k_{22} - k_{33}} \quad \text{and} \quad \delta_{31} = \frac{\Delta_{31}}{k_{33} - k_{11}}$$

Therefore, to the first order of small quantities Δ_{ij}:

$$\delta \equiv \begin{pmatrix} k_{11} + \Delta_{11} & \Delta_{12} & \Delta_{31} \\ \Delta_{12} & k_{22} + \Delta_{22} & \Delta_{23} \\ \Delta_{31} & \Delta_{23} & k_{33} + \Delta_{33} \end{pmatrix}\delta_c = \begin{pmatrix} k_{11} + \Delta_{11} & 0 & 0 \\ 0 & k_{22} + \Delta_{22} & 0 \\ 0 & 0 & k_{33} + \Delta_{33} \end{pmatrix}$$

where $\delta = \begin{pmatrix} 1 & \dfrac{\Delta_{12}}{k_{11} - k_{22}} & \dfrac{-\Delta_{31}}{k_{33} - k_{11}} \\ \dfrac{-\Delta_{12}}{k_{11} - k_{22}} & 1 & \dfrac{\Delta_{23}}{k_{22} - k_{33}} \\ \dfrac{\Delta_{31}}{k_{33} - k_{11}} & \dfrac{-\Delta_{23}}{k_{22} - k_{33}} & 1 \end{pmatrix}$ is the transformation $x' = x$ ..... (21.18)

The electro and piezo-optic effects of biaxial crystals can be handled by these infinitesimal transformations, but uniaxial crystals and cubic crystals may require finite rotations to re-diagonalize the k^{-1} matrix. In the case of cubic crystals we note that $\begin{pmatrix} k & 0 & 0 \\ 0 & k & \Delta \\ 0 & \Delta & k \end{pmatrix}$ may be diagonalized by a rotation of 45° about x_1, giving

$$\begin{pmatrix} k & 0 & 0 \\ 0 & k + \Delta & 0 \\ 0 & 0 & k - \Delta \end{pmatrix} \text{ ..... (21.19)}$$

$\begin{pmatrix} k & 0 & \Delta_2 \\ 0 & k & \Delta_1 \\ \Delta_2 & \Delta_1 & k \end{pmatrix}$ becomes $\begin{pmatrix} k & 0 & \sqrt{\Delta_1^2 + \Delta_2^2} \\ 0 & k & 0 \\ \sqrt{\Delta_1^2 + \Delta_1^2} & 0 & k \end{pmatrix}$ upon rotation through angle

$\tan^{-1}\frac{\Delta_1}{\Delta_2}$ about x_3 and diaonalizes by then rotating through 45° about x_2 giving:

$$k'' = \begin{pmatrix} k + \sqrt{\Delta_1^2 + \Delta_2^2} & 0 & 0 \\ 0 & k & 0 \\ 0 & 0 & k - \sqrt{\Delta_1^2 + \Delta_2^2} \end{pmatrix} \quad \ldots\ldots (21.20)$$

The work can be handled with single column matrices K instead of using the square matrices k. If k is a diagonal single column matrix (i.e., the single column matrix of a diagonal matrix), than the almost diagonal matrix $K + \Delta$ is diagonalized by the transformation:

$$\begin{pmatrix} 1 & 0 & 0 & 0 & \frac{2\Delta_5}{K_1 - K_3} & \frac{2\Delta_6}{K_1 - K_2} \\ 0 & 1 & 0 & \frac{2\Delta_4}{K_2 - K_3} & 0 & \frac{-2\Delta_6}{K_1 - K_2} \\ 0 & 0 & 1 & \frac{-2\Delta_4}{K_2 - K_3} & \frac{-2\Delta_5}{K_1 - K_3} & 0 \\ 0 & \frac{-\Delta_4}{K_2 - K_3} & \frac{\Delta_4}{K_2 - K_3} & & \frac{-\Delta_6}{K_1 - K_2} & \frac{-\Delta_5}{K_1 - K_3} \\ \frac{-\Delta_5}{K_1 - K_3} & 0 & \frac{\Delta_5}{K_1 - K_3} & \frac{\Delta_6}{K_1 - K_2} & 1 & \frac{\Delta_4}{K_1 - K_3} \\ \frac{-\Delta_6}{K_1 - K_2} & \frac{\Delta_6}{K_1 - K_2} & 0 & \frac{\Delta_5}{K_1 - K_3} & \frac{\Delta_4}{K_2 - K_3} & 1 \end{pmatrix} \begin{pmatrix} K_1 + \Delta_1 \\ K_2 + \Delta_2 \\ K_1 + \Delta_3 \\ \Delta_4 \\ \Delta_5 \\ \Delta_6 \end{pmatrix} =$$

$$\begin{pmatrix} K_1 + \Delta_1 \\ K_2 + \Delta_2 \\ K_3 + \Delta_3 \\ 0 \\ 0 \\ 0 \end{pmatrix} \quad \ldots\ldots\ldots\ldots\ldots\ldots (21.21)$$

which transforms vectors as $x' = \delta x$ where

$$\delta = \begin{pmatrix} 1 & \frac{\Delta_6}{K_1 - K_2} & \frac{\Delta_5}{K_1 - K_3} \\ \frac{-\Delta_6}{K_1 - K_2} & 1 & \frac{\Delta_4}{K_2 - K_3} \\ \frac{-\Delta_5}{K_1 - K_3} & \frac{-\Delta_4}{K_2 - K_3} & 1 \end{pmatrix} \quad \ldots\ldots\ldots (21.22)$$

If K_1, K_2 and K_3 are not all different the preceding analysis falls down as some terms become infinite; a finite transformation is needed in this case. The difficulty can generally be doged by applying a 45° rotation about one of the axes. Sometimes the easiest solution is to rotate through an angle ϕ about a coordinate axis then solve for the value of ϕ that will vanish certain terms. As examples of these devices we give the following:

$$\begin{pmatrix} K_1 \\ K_1 \\ K_1 \\ \Delta_4 \\ 0 \\ 0 \end{pmatrix} \text{ rotated 45° about } x_1 \text{ becomes } \begin{pmatrix} K_1 \\ K_1 + \Delta_4 \\ K_1 - \Delta_4 \\ 0 \\ 0 \\ 0 \end{pmatrix} \quad \ldots\ldots (21.23)$$

$$\begin{pmatrix} K_1 \\ K_1 \\ K_1 \\ \Delta_4 \\ \Delta_5 \\ 0 \end{pmatrix} \text{ rotated through } \tan^{-1}\frac{\Delta_4}{\Delta_5} \text{ about } x_3 \text{ is } \begin{pmatrix} K_1 \\ K_1 \\ K_1 \\ 0 \\ \sqrt{\Delta_4^2 + \Delta_5^2} \\ 0 \end{pmatrix} \text{ and rotated 45° about } x_2' \text{ is } \begin{pmatrix} K + \sqrt{\Delta_4^2 + \Delta_5^2} \\ K \\ K - \sqrt{\Delta_4^2 + \Delta_5^2} \\ 0 \\ 0 \\ 0 \end{pmatrix} \quad . (21.24)$$

D = electric induction
E = electric field
k = dielectric constant matrix (square)
K = dielectric constant matrix (single column)
a = transformation matrix for vectors
α = transformation matrix for tensors (of stress tensor sort)
X = stress matrix (single column)
e = strain matrix (square)
ϵ = strain matrix (single column)
S = elastic modulus matrix
C = elastic constant matrix
H = temperature change of elastic modulus matrix

h = temperature change of elastic constant matrix
T_S = temperature coefficient of elastic modulus terms
T_C = temperature coefficient of elastic constant terms
A = temperature expansion matrix
d = piezo-electric constant matrix
g = inverse piezo effect matrix
G = electro-striction matrix
Z = electro-optic matrix
π = stress optic matrix
m = strain optic matrix
P = polarization = elec. mom. per unit vol. = surface charge per unit area
η = susceptibility = $\frac{P}{E}$

Table of Equations	Transformations
$D = \frac{1}{4\pi} kE$ $e = SX$ $X = Ce$ $S = C^{-1}$ $h = -C^{\circ}HC^{\circ}$ $H = -S^{\circ}hS^{\circ}$ $\Delta l = tAl + l^2Bl$ $D = dX$ $e = gE$ $g = d_c$ $K^{-1} = K^{-1^{\circ}} + ZE$ $K^{-1} = K^{-1^{\circ}} + \pi X$ $K^{-1} = K^{-1^{\circ}} + me$ $P = \frac{k - I}{4\pi} E = \pi E$ $\pi = \frac{k - I}{4\pi}$	The form $\begin{matrix} & x & y & z \\ x' & l_1 & m_1 & n_1 \\ y' & l_2 & m_2 & n_2 \\ z' & l_3 & m_3 & n_3 \end{matrix}$ is the transformation $a = \begin{matrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \\ n_1 & n_2 & n_3 \end{matrix}$ $A' = aAa^{-1}$ $D' = aD$ $E' = aE$ $k' = aka_c$ $K' = \alpha K$ $X' = \alpha X$ $e' = \alpha_c^{-1}e$ $C' = \alpha C\alpha_c$ $S' = \alpha_c^{-1}S\alpha^{-1}$ $h' = \alpha h\alpha_c$ $H = \alpha_c^{-1}H\alpha^{-1}$ $h_{ij} = C^{\circ}_{ij}T_{C_{ij}}$ $H_{ij} = S^{\circ}_{ij}T_{S_{ij}}$ $d' = ad\alpha^{-1}$

References as to Crystal Data

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